

## Supporting Information

Theoretical investigation and design of high-efficiency  
dithiafulvenyl-based sensitizers for dye-sensitized solar cells:  
The impacts of elongating  $\pi$ -spacers and rigidifying dithiophene

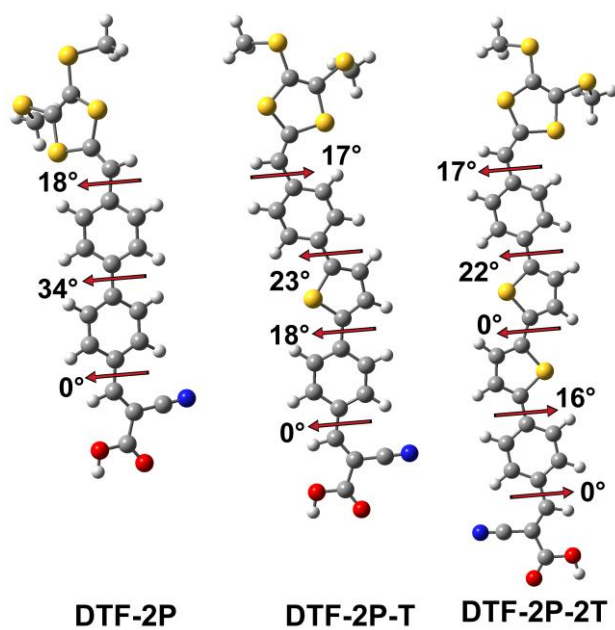
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State Key Laboratory of Theoretical and Computational Chemistry,

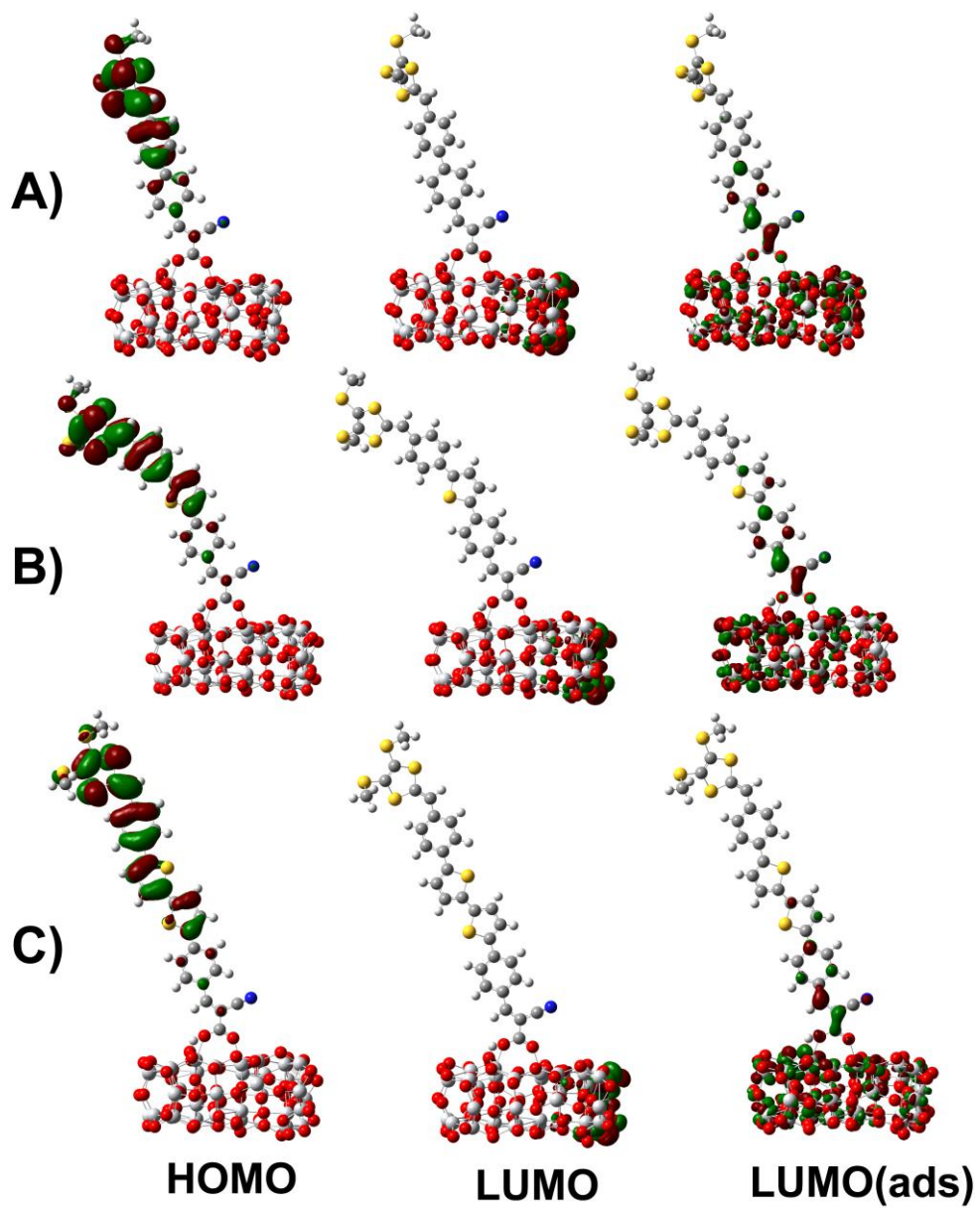
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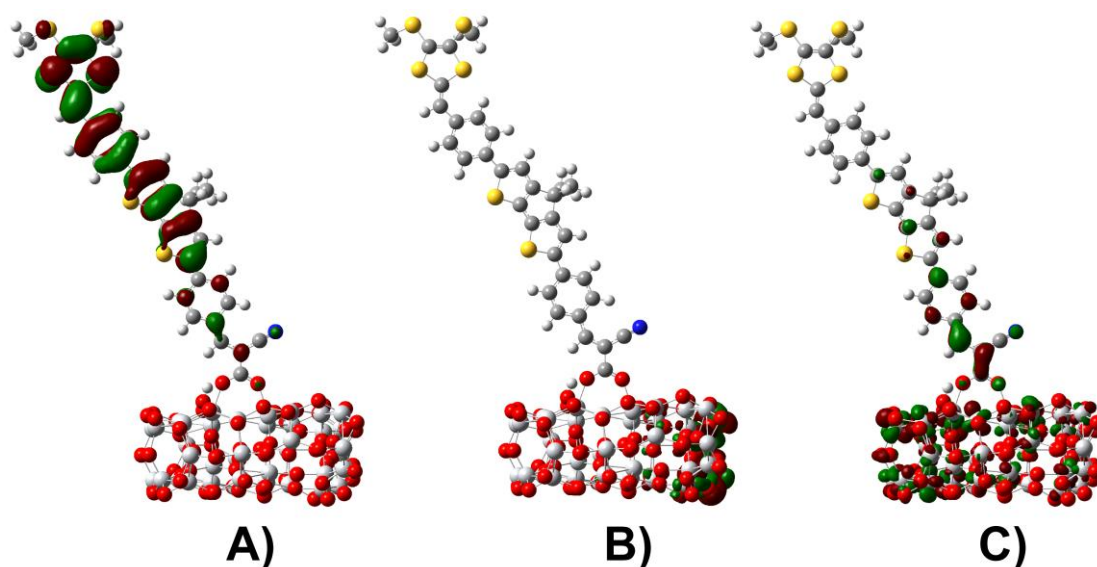


**Figure S1** Optimized ground state geometries along with the selected dihedral angle values of of DTF-2P, DTF-2P-T, and DTF-2P-2T.



**Figure S2** Selected molecular orbitals for the HOMO , LUMO , and LUMO(ads) of DTF-2P/TiO<sub>2</sub>

(A), DTF-2P-T/TiO<sub>2</sub> (B), and DTF-2P-2T/TiO<sub>2</sub> (C) systems. (LUMO(ads) refers to the dye contribution to the LUMOs of dye/TiO<sub>2</sub> system)



**Figure S3** Some selected molecular orbitals for the HOMO (A), LUMO (B), and LUMO(ads) (C) of DTF-2P-2T-C/TiO<sub>2</sub> systems.

**Table S1.** Basis set effect on the maximum absorption wavelength (nm/eV) for DTF-2P and DTF-2P-T

Dyes	6-31G(d)	6-311+G(d,p)	expt <sup>1</sup>
DTF-2P	397/3.13	415/2.99	406/3.05
DTF-2P-2T	434/2.86	452/2.74	427/2.90

**Table S2.** Comparison of the excitation energies (nm/eV) for DTF-2P and DTF-2P-T, calculated within TDDFT using different functionals (BhandH and CAM-B3LYP) with 6-31G(d) basis set in THF solution.

	BHandH	CAM-B3LYP	expt. <sup>1</sup>
DTF-2P	397/3.13	387/3.20	406/3.05
DTF-2P-T	434/2.86	424/2.92	427/2.90

**Table S3** Absorption spectra data for the designed dyes (DTF-2P-2T-C, DTF-2P-2T-Bi, DTF-2P-2T-S)

	$\lambda_{max}$ (nm/eV)	$f$	assign.
DTF-2P-2T-C	498/2.49	2.5955	H→L (75%)
DTF-2P-2T-S	453/2.73	2.7152	H→L (62%)
DTF-2P-2T-Bi	443/2.80	2.5658	H→L (63%)

1. K. P. Guo; K. Y. Yan; X. Q. Lu; Y. C. Qiu; Z. K. Liu; J. W. Sun; F. Yan; W. Y. Guo; S. H. Yang, *Org Lett* 2012, **14**, 2214.

Cartesian coordinates:

DTF-2P

0 1

C	1.04236300	-1.92715700	-0.13250600
C	-0.31376700	-2.21167200	-0.17713100
C	-1.26742100	-1.23036700	-0.52615500
C	-0.77649700	0.04732800	-0.86477900
C	0.58407800	0.32871000	-0.82648900
C	1.52711800	-0.64479200	-0.45353300
H	1.74141100	-2.71809300	0.12338600
H	-0.65501600	-3.21510000	0.06560200
H	-1.45395000	0.82839200	-1.19138900
H	0.91809700	1.33268800	-1.07217700
C	7.16487000	0.60175000	-0.36937900
C	8.23438700	0.20613200	0.38119700
H	7.41059800	1.32220300	-1.14471900
C	9.60030000	0.73923800	0.12647200
O	10.58670900	0.42362200	0.75658200
O	9.64244300	1.63088500	-0.89840000
H	10.57600600	1.90291400	-0.96665500
C	-2.67375300	-1.61130400	-0.52394900
C	-3.78834400	-0.84033300	-0.50950000
H	-2.84964500	-2.68604500	-0.50991600
C	8.16739800	-0.73307900	1.45748300
N	8.09885400	-1.49905600	2.33105000
S	-5.40402600	-1.58806500	-0.60754300
S	-3.88901900	0.93187500	-0.43085900
C	-6.32319900	-0.15015200	-0.10937400
C	-5.62799400	1.01065000	-0.03016000
S	-8.07461300	-0.29981400	0.08322900
S	-6.30848700	2.60875200	0.29527600
C	-8.21139700	-1.70426500	1.25971300
H	-7.70069500	-1.47773900	2.19806600
H	-9.28199000	-1.81834500	1.45004700
H	-7.82437400	-2.63203200	0.83375200
C	-5.51839900	3.02326200	1.90301800
H	-5.85555600	2.34058200	2.68586500
H	-4.42930400	3.00287500	1.82653800
H	-5.84373500	4.03937200	2.14205600
C	2.97242700	-0.33906700	-0.41225900
C	3.55403400	0.56761800	-1.31872400
C	3.81913400	-0.94651700	0.53708200
C	4.91097600	0.84723600	-1.27347800

H	2.93918700	1.03255000	-2.08314100
C	5.17720300	-0.67111900	0.58646400
H	3.39601700	-1.62746000	1.26914900
C	5.76089200	0.23776300	-0.32400600
H	5.33634100	1.54370400	-1.99201500
H	5.78326800	-1.15628800	1.34105800

DTF-2P-T

0 1

C	-1.09278500	-0.42664500	-0.27281800
C	-2.46384300	-0.42293700	-0.49601600
C	-3.22650200	-1.60383400	-0.38604000
C	-2.52523700	-2.79140500	-0.07851000
C	-1.15709400	-2.79744400	0.13701300
C	-0.40399900	-1.60822500	0.05603900
H	-0.54772200	0.51060100	-0.34673300
H	-2.93269200	0.51073300	-0.78545500
H	-3.07707300	-3.72586400	-0.01059300
H	-0.65600100	-3.73730100	0.34819100
C	8.72737500	1.25322800	-0.26014400
C	10.01236200	0.82178900	-0.08946300
H	8.64744600	2.28555400	-0.58957900
C	11.17166500	1.71794900	-0.34567400
O	12.33188400	1.39301100	-0.21004200
O	10.80476500	2.96129100	-0.75479800
H	11.63961300	3.44648300	-0.88809700
C	-4.66757700	-1.69004900	-0.57723000
C	-5.60999200	-0.71584400	-0.58421200
C	10.37564900	-0.49234600	0.34094100
N	10.65585900	-1.56583800	0.69292500
S	-5.38332200	1.02405300	-0.30274900
S	-7.31296500	-1.10774300	-0.93841900
C	-7.11122200	1.40798100	-0.06194300
C	-7.99803700	0.42453600	-0.35110300
S	-7.51339100	3.06699800	0.39525300
S	-9.75687900	0.60652700	-0.34298000
C	-6.82583000	3.15518300	2.09802400
H	-5.75489800	2.94217100	2.10546200
H	-6.99094800	4.18272900	2.43325300
H	-7.35291400	2.46756200	2.76281000
C	-10.28432200	-0.83861600	0.66162000
H	-10.02493100	-1.78417300	0.18145900
H	-9.85351400	-0.79367300	1.66413800
H	-11.37256900	-0.76038900	0.73247900

C	4.84385000	-0.52642100	0.20495700
C	5.02139800	0.81136300	-0.20296800
C	6.00466000	-1.29104900	0.45857700
C	6.28984700	1.34839300	-0.34464700
H	4.15527800	1.43853800	-0.39303600
C	7.27304400	-0.75327000	0.32613800
H	5.90646300	-2.33281200	0.74606700
C	7.45185500	0.58879400	-0.08241000
H	6.39588000	2.38410000	-0.65774600
H	8.13036000	-1.38204900	0.53034800
C	1.03737600	-1.62376200	0.29966500
C	1.77827700	-2.54159700	1.01855800
S	2.09292500	-0.38864400	-0.35613600
C	3.16313300	-2.25785400	1.05408400
H	1.33024900	-3.38016200	1.53972400
C	3.51932100	-1.11469600	0.36499400
H	3.87586500	-2.86109600	1.60533300
H	-5.04424000	-2.70289300	-0.71387800

DTF-2P-2T

0 1

C	2.73602600	-1.72219500	0.15599200
C	4.08439700	-2.04055400	0.12683400
C	5.05714700	-1.11928200	-0.31904200
C	4.58962900	0.13143800	-0.77529400
C	3.23824700	0.44832900	-0.75410900
C	2.27619100	-0.46283300	-0.27716400
H	2.02836000	-2.45265300	0.53898900
H	4.40563400	-3.01895600	0.47558200
H	5.27799200	0.85356400	-1.20023600
H	2.91746800	1.40862100	-1.14655600
C	-11.16143300	0.93590200	-0.01437000
C	-12.32887700	0.27930400	0.25546700
H	-11.29331200	1.97995300	-0.28488700
C	-13.64361900	0.97024200	0.17419100
O	-14.71091000	0.44080300	0.39936000
O	-13.53825900	2.27754400	-0.18343200
H	-14.45259000	2.61486400	-0.20244900
C	6.45449500	-1.52840000	-0.29047900
C	7.58484200	-0.78439100	-0.36543900
H	6.60904500	-2.59986700	-0.16984700
C	-12.41629200	-1.09734300	0.63121800
N	-12.47151400	-2.21934300	0.93599900
S	9.18512600	-1.57030800	-0.40622100

S	7.72101100	0.98477500	-0.47002200
C	10.13618400	-0.10877500	-0.05755900
C	9.46431700	1.06792600	-0.08986000
S	11.88546700	-0.27764700	0.13959800
S	10.17735200	2.67693600	0.07321400
C	11.99756600	-1.51758600	1.49076100
H	11.57047400	-2.47849300	1.19717200
H	13.06692600	-1.64451400	1.67993000
H	11.51211400	-1.14987600	2.39730700
C	9.40029800	3.26481800	1.63240900
H	8.31077600	3.25741100	1.56004600
H	9.72704300	2.65733200	2.47908700
H	9.74536900	4.29337300	1.76855100
C	-7.00605000	-0.16003600	-0.06318100
C	-7.45276500	1.13911700	-0.38155600
C	-7.98432300	-1.11770100	0.28869100
C	-8.80036600	1.45490800	-0.35088300
H	-6.73663900	1.90228600	-0.67222000
C	-9.33219300	-0.80552800	0.31277200
H	-7.67669500	-2.12046700	0.56656700
C	-9.78070800	0.49694500	-0.00807500
H	-9.11479500	2.46410800	-0.60507600
H	-10.04081000	-1.57494200	0.59196100
C	0.86082500	-0.10096400	-0.24809200
C	0.29356200	1.15772100	-0.23531700
S	-0.39865800	-1.32403400	-0.23155900
C	-1.12031800	1.15149600	-0.20472800
H	0.88292200	2.06753700	-0.21775100
C	-1.67190000	-0.11526500	-0.19276000
H	-1.71954700	2.05583500	-0.18033400
C	-3.06146800	-0.50134400	-0.15681200
C	-3.61214000	-1.77029200	-0.13693000
S	-4.33301400	0.70621600	-0.12584300
C	-5.02396400	-1.77695100	-0.09928600
H	-3.01175200	-2.67355300	-0.15474600
C	-5.59432700	-0.51836300	-0.09151600
H	-5.60846600	-2.68998400	-0.10247600

DTF-2P-2T-C

0 1

C	2.86623500	-1.90873600	0.16435000
C	4.21226700	-2.23388300	0.11649400
C	5.18571100	-1.31243500	-0.32750800
C	4.71994600	-0.05349300	-0.76239100



C	3.37054500	0.26985600	-0.72443000
C	2.40710000	-0.64181000	-0.24922400
H	2.15955700	-2.64056100	0.54665700
H	4.53148900	-3.21846000	0.44946700
H	5.40785600	0.67033600	-1.18536100
H	3.05152500	1.23618600	-1.10329100
C	-11.08702100	-0.82825900	0.26000100
C	-12.19777300	-0.04391800	0.11535000
H	-11.30706800	-1.87037900	0.47486200
C	-13.56678700	-0.60729800	0.24766600
O	-14.58815300	0.03655600	0.13251400
O	-13.57256300	-1.94062800	0.51580400
H	-14.51368600	-2.18637400	0.57845200
C	6.58086700	-1.72966800	-0.32017600
C	7.71453300	-0.99097900	-0.39586700
H	6.73058700	-2.80385900	-0.21885700
C	-12.16810800	1.35688300	-0.16767900
N	-12.12646500	2.49727500	-0.39772000
S	9.30972800	-1.78523000	-0.46961000
S	7.86011400	0.77914800	-0.47145800
C	10.27267000	-0.33608500	-0.10251900
C	9.60747500	0.84482000	-0.10604600
S	12.02291700	-0.51770500	0.07365800
S	10.33134400	2.44642000	0.08071900
C	12.14251600	-1.79421000	1.38961100
H	11.70997500	-2.74562400	1.07390500
H	13.21307700	-1.92928800	1.56593800
H	11.66610100	-1.44991500	2.31004800
C	9.58003600	3.00450400	1.66328700
H	8.48949200	2.99884000	1.60794200
H	9.91963700	2.38049900	2.49272700
H	9.92792800	4.03008600	1.81395700
C	-6.84478700	-0.15063600	0.07021500
C	-7.40335200	-1.41874400	0.34100300
C	-7.74439400	0.91979100	-0.14786400
C	-8.77443300	-1.59769300	0.39064200
H	-6.75373100	-2.26871500	0.52930400
C	-9.11488700	0.74364300	-0.09116700
H	-7.35726500	1.90568300	-0.38308300
C	-9.67379900	-0.52758200	0.18068900
H	-9.17259000	-2.58662300	0.60422400
H	-9.75753700	1.59678600	-0.26817600
C	0.99465900	-0.27485300	-0.20308100
C	0.43423800	0.99302400	-0.17306800

S	-0.26628300	-1.51992900	-0.18940200
C	-0.97629400	0.97553600	-0.13290600
H	1.03946600	1.89266100	-0.15088900
C	-1.49948900	-0.30943500	-0.13190200
C	-2.93131200	-0.23196800	-0.07897400
C	-3.31598600	1.10319600	-0.04859700
S	-4.28140500	-1.30622500	-0.04637500
C	-4.71253300	1.26704500	0.00356200
C	-5.40815100	0.06376800	0.01522600
H	-5.21239100	2.22804700	0.05373700
C	-2.09214200	2.01878000	-0.07657700
C	-1.99881700	2.88026000	1.20251000
H	-1.07729800	3.47357200	1.19976400
H	-2.84555700	3.57357600	1.26196300
H	-2.00237500	2.25486600	2.10040000
C	-2.08642300	2.91991900	-1.33158600
H	-1.16513100	3.51200500	-1.37461900
H	-2.15442500	2.32305000	-2.24620100
H	-2.93313600	3.61552400	-1.31016800

#### DTF-2P-2T-S

0 1

C	2.75633700	-1.69374100	0.13179400
C	4.08728700	-2.07517500	0.07195600
C	5.09623400	-1.18901200	-0.36401900
C	4.68278300	0.09456100	-0.77923700
C	3.34838600	0.47436000	-0.72951300
C	2.35138500	-0.40278200	-0.26088900
H	2.02079500	-2.39967200	0.50824900
H	4.36611200	-3.07700600	0.38908800
H	5.39884600	0.79368700	-1.19692700
H	3.06802300	1.45811600	-1.09396100
C	-11.09588900	-0.86991100	0.28213400
C	-12.24485400	-0.15807800	0.08418400
H	-11.26035100	-1.90890200	0.55410300
C	-13.58358500	-0.78860700	0.23829300
O	-14.63614800	-0.20890500	0.07733700
O	-13.51802500	-2.10163500	0.58364800
H	-14.44418000	-2.39741000	0.65386400
C	6.47285900	-1.66411600	-0.36966800
C	7.63534400	-0.96988800	-0.42909700
H	6.57863900	-2.74546700	-0.29262400
C	-12.28951900	1.22405400	-0.27872000
N	-12.30911500	2.34985500	-0.57359500

S	9.19702100	-1.82536100	-0.52096800
S	7.85153300	0.79412400	-0.46156600
C	10.21711600	-0.42514800	-0.11963700
C	9.59978200	0.78122100	-0.09498700
S	11.95831600	-0.68167200	0.05231200
S	10.38753000	2.34756700	0.12795500
C	12.02463500	-1.98346900	1.34712200
H	11.54840500	-2.90904600	1.01775800
H	13.08856200	-2.16964300	1.51687300
H	11.56737500	-1.63298900	2.27490600
C	9.64558000	2.90823700	1.71404900
H	8.55632800	2.94971800	1.64962700
H	9.95110000	2.25613500	2.53506900
H	10.03482600	3.91544200	1.88588000
C	-6.89812300	0.02960300	0.09083100
C	-7.38565200	-1.25029600	0.42585600
C	-7.84835500	1.03563700	-0.19607300
C	-8.74640600	-1.50188500	0.47331300
H	-6.69086300	-2.04846700	0.67074100
C	-9.20875000	0.78775800	-0.14050200
H	-7.50989500	2.02426000	-0.48877900
C	-9.69845300	-0.49537700	0.19721600
H	-9.09272600	-2.49759900	0.73880500
H	-9.89530900	1.59217400	-0.37212500
C	0.95421900	0.02189000	-0.19980500
C	0.45677900	1.30691100	-0.12657000
S	-0.35389000	-1.17630000	-0.22553700
C	-0.95842400	1.33789700	-0.08505100
H	1.09074100	2.18380700	-0.07271700
C	-1.55554500	0.07707100	-0.12262600
C	-2.96853400	0.14359300	-0.06577000
C	-3.44246200	1.45550200	0.01151500
S	-4.28161400	-0.99385300	-0.07101300
C	-4.85085600	1.55441600	0.07023800
C	-5.47085500	0.31961800	0.04001300
H	-5.39326300	2.48802500	0.16009000
S	-2.13894200	2.63869000	0.02327100

DTF-2P-2T-Bi

0 1

C	-2.33076100	-0.10923000	-0.72451100
C	-3.70459400	-0.30868000	-0.74011400
C	-4.29025200	-1.42703100	-0.10999100
C	-3.41306300	-2.34584600	0.50625300

C	-2.04245900	-2.14274200	0.53077100
C	-1.46413700	-1.01182700	-0.07862800
H	-1.91719100	0.74421000	-1.25355300
H	-4.31774300	0.39152800	-1.29671800
H	-3.82736700	-3.22586300	0.99198000
H	-1.41070000	-2.86029100	1.04743900
C	-5.71892000	-1.70591400	-0.06622200
C	-6.77502100	-0.88349300	-0.27864200
S	-6.74794000	0.85862200	-0.62962800
S	-8.43881600	-1.52430100	-0.25521500
C	-8.48175400	1.14629400	-0.30957500
C	-9.25802200	0.04918400	-0.13411100
S	-9.04947600	2.81802100	-0.38885200
S	-11.01764800	0.06788100	0.03924700
C	-8.25253600	3.54583000	1.09970200
H	-7.16710800	3.43201600	1.06338400
H	-8.50404700	4.60975300	1.08342200
H	-8.65005500	3.09275900	2.01037800
C	-11.26751100	-1.00395000	1.51024800
H	-10.94168500	-2.02970300	1.32688000
H	-10.75313800	-0.59474800	2.38240000
H	-12.34565900	-0.99884700	1.69189500
H	-5.97192200	-2.73115200	0.20066600
C	-0.02165100	-0.77559500	-0.05918900
C	0.64297400	0.42594200	-0.19818900
S	1.11034000	-2.12435200	0.15189900
C	2.04924300	0.27086200	-0.13024000
H	0.13253900	1.37489700	-0.30997600
C	2.47517000	-1.04291900	0.06074900
C	3.87855100	-1.19541000	0.13938800
S	3.41071000	1.35339000	-0.21765300
C	4.54586100	0.00765300	0.00978500
C	5.98440000	0.24133300	0.04270500
C	6.52479300	1.52433100	0.26589100
C	6.89235300	-0.82457700	-0.14919400
C	7.89488000	1.72251900	0.29779400
H	5.86338500	2.36914700	0.43463900
C	8.26183900	-0.62958600	-0.10905500
H	6.51345200	-1.82051400	-0.35429200
C	8.80441100	0.65695200	0.11597300
H	8.28233800	2.72261800	0.47559800
H	8.91430200	-1.47935800	-0.26472600
C	10.21621000	0.97898300	0.17287000
C	11.33434000	0.20499500	0.04281800

H	10.42399600	2.03014600	0.35280000
C	11.32098900	-1.20452300	-0.19625900
N	11.29361100	-2.35185300	-0.39033800
C	12.69840000	0.78983500	0.14484600
O	13.72557000	0.15429500	0.04004300
O	12.68880200	2.13015700	0.37116100
H	13.62680600	2.39122600	0.41754500
H	4.38240500	-2.13894500	0.31097600

1. K. P. Guo; K. Y. Yan; X. Q. Lu; Y. C. Qiu; Z. K. Liu; J. W. Sun; F. Yan; W. Y. Guo; S. H. Yang, *Org Lett* 2012, **14**, 2214.