Electronic Supporting Information

Influence of substitution pattern and enhanced π-conjugation on a family of thiophene functionalized 1,5-dithia-2,4,6,8-tetrazocines

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Table S1 – Molar coefficients of extinction of **1c**, **2a** and **2b** in DCM.

1c		**2a**		**2b**	
λ (nm)	ε ($M^{-1}cm^{-1}$)	λ (nm)	ε ($M^{-1}cm^{-1}$)	λ (nm)	ε ($M^{-1}cm^{-1}$)
269	15230	256	14401	259	16501
343	39396	299	11880	304	12527
360	33231	395	59436	404	66223
458	4563	477	3056	485	2944

Table S2 – Comparative table for the measured molar coefficients of extinction[a] with the corresponding calculated oscillator strengths.[b]

	λ (nm)	ε ($M^{-1}cm^{-1}$)	Calculated λ (nm)	*f*
1c	343	39396	346	1.0581
	458	4563	516	0.0382
2a	395	59436	415	1.5882
	477	3056	594	0.0175
2b	404	66223	426	1.6323
	485	2944	624	0.0139

[a] Optical measurements were performed on dilute DCM solutions. [b] TD DFT/B3LYP/6-311+G(d,p) level of theory on geometry optimized structures (where R = Me for **1c** and **2b**) where *k* = order of excitation energy and *f* = oscillator strength.

Table S3 – TD DFT optical transitions[a] for **1c**, **2a** and **2b**.

k	**1c**		**2a**		**2b**	
	E (eV)	*f*	E (eV)	*f*	E (eV)	*f*
1	2.4026	0.0382	2.0858	0.0175	1.9857	0.0139
2	2.8539	0.0011	2.3665	0.0041	2.2337	0.0047
3	3.1997	0.0000	2.9835	1.5882	2.9068	1.6323
4	3.2019	0.0037	3.2132	0.0006	3.2088	0.0013
5	3.2408	0.0026	3.4519	0.0199	3.3413	0.0606
6	3.5839	1.0581	3.4649	0.0852	3.4151	0.0664
7	4.0145	0.0000	3.4961	0.0403	3.4466	0.0767
8	4.2491	0.0137	3.5875	0.0751	3.4810	0.0130
9	4.3360	0.0102	3.6050	0.0802	3.5372	0.1052
10	4.4070	0.1824	3.6877	0.0034	3.6214	0.0067
11	4.4152	0.1217	3.6896	0.0009	3.6300	0.0000
12	4.4734	0.0246	3.9833	0.0003	3.8247	0.0002
13	4.5689	0.0901	3.9870	0.2722	3.8710	0.2592
14	4.6559	0.0075	4.0327	0.0000	4.0307	0.0000
15	4.7257	0.0000	4.2650	0.0059	4.1824	0.0284
16	5.0160	0.0142	4.3402	0.0025	4.2953	0.0013
17	5.1285	0.0472	4.3488	0.0114	4.3442	0.0104
18	5.3278	0.0000	4.4521	0.0057	4.4141	0.0015
19	5.3768	0.0000	4.4701	0.0823	4.4430	0.0607
20	5.4301	0.0681	4.5227	0.0001	4.4589	0.0048

[a] TDDFT/B3LYP/6-311+G(d,p) level of theory on geometry optimized structures (where R = Me for **1c** and **2b**) where *k* = order of excitation energy and *f* = oscillator strength.

Table S4 – Selected TD DFT transitions for **1c**, **2a** and **2b** (DCM solvent cavity; where R = Me for **1c** and **2b**)

Compound	Calculated λ (nm)	Transition	Oscillator strength (*f*)
1c	346	HOMO →LUMO+1	1.0581
	281	HOMO-6→LUMO HOMO-5→LUMO+1 HOMO-2→LUMO+1	0.1824
	281	HOMO-6→LUMO+1 HOMO-5→LUMO	0.1217
	271	HOMO-6→LUMO HOMO-3→LUMO+1 HOMO-2→LUMO+1 HOMO →LUMO+2	0.0901
2a	416	HOMO →LUMO+1	1.5882
	358	HOMO-5→LUMO HOMO-3→LUMO	0.0852
	311	HOMO-9→LUMO HOMO-1→LUMO+2	0.2722
	277	HOMO-9→LUMO HOMO-6→LUMO+1 HOMO-4→LUMO+1 HOMO-3→LUMO+2 HOMO-2→LUMO+1	0.0823
2b	426	HOMO →LUMO+1	1.6323
	360	HOMO-5→LUMO HOMO-3→LUMO	0.0767
	350	HOMO-6→LUMO HOMO-4→LUMO HOMO →LUMO+2	0.1052
	320	HOMO-1→LUMO+2	0.2592

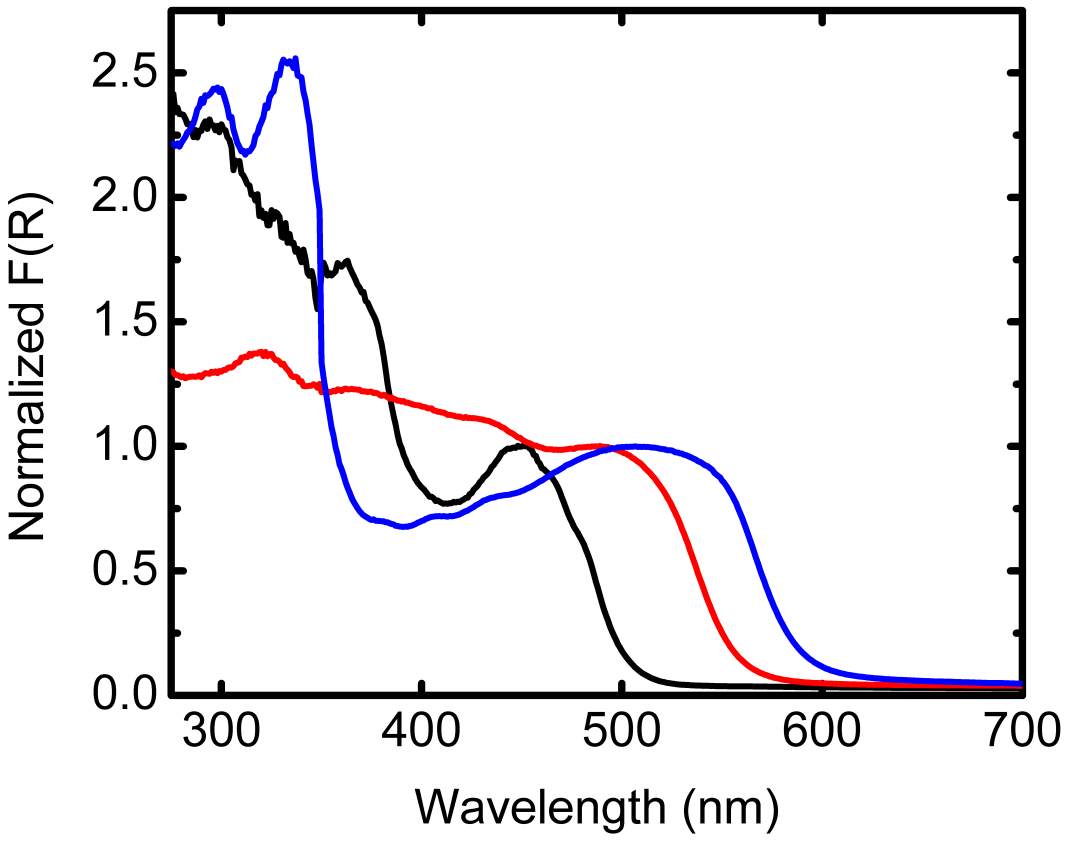


Figure S1 – Solid-state diffuse reflectance measurements of **1c** (black), **2a** (red) and **2b** (blue). Results are presented in Kubelka-Munk units (F(R)) so as to directly compare with solution absorption measurements.

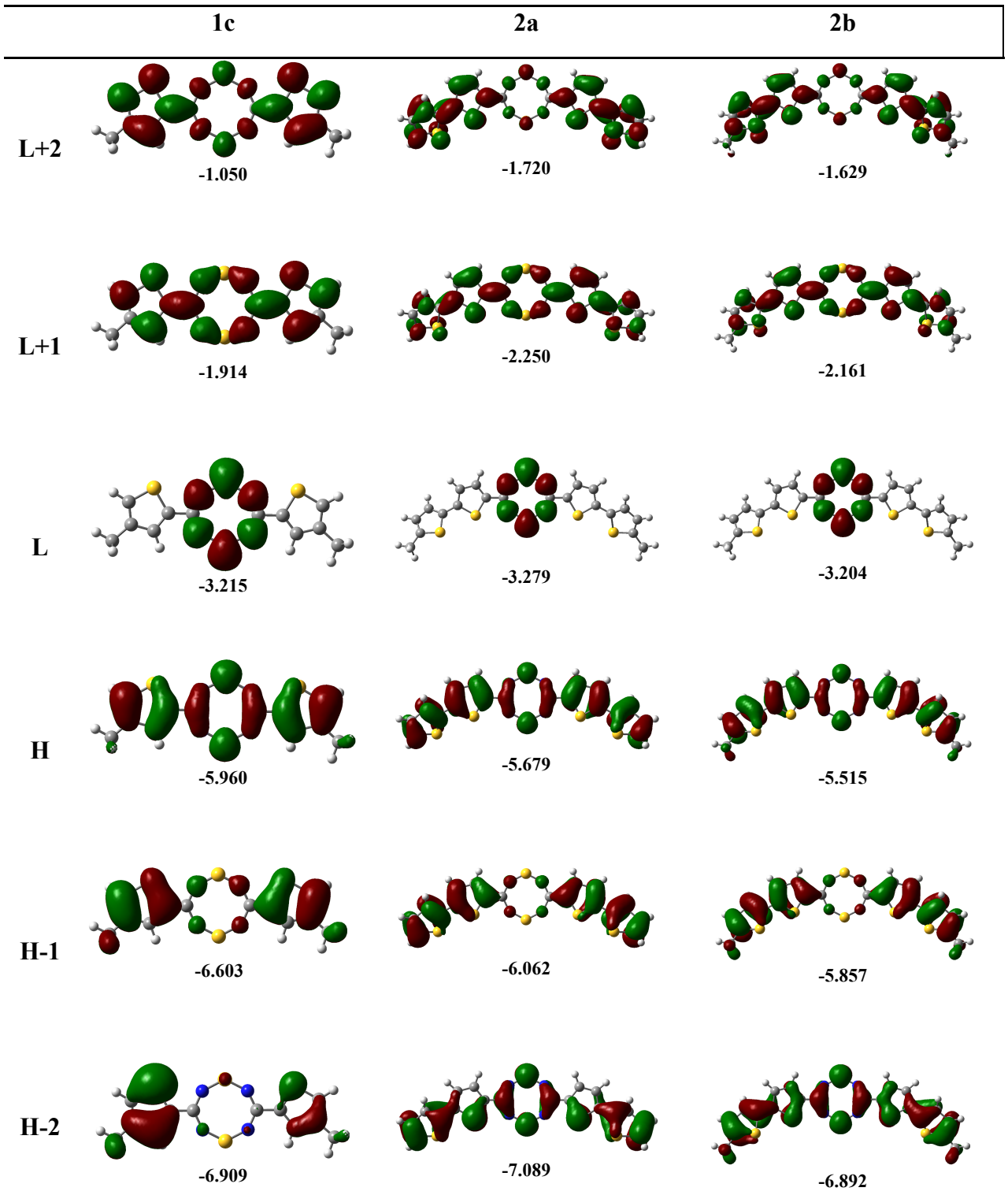


Figure S2 – Frontier molecular orbitals and corresponding energies (in eV) for **1c**, **2a** and **2b**.

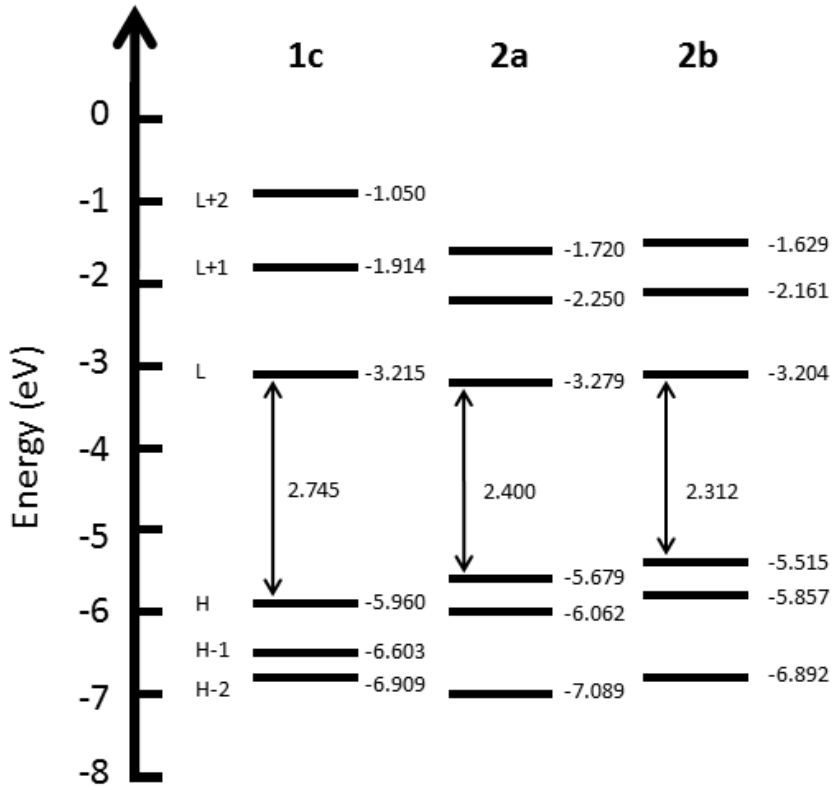


Figure S3 – Energy level diagram for the frontier orbitals of **1c**, **2a** and **2b**.

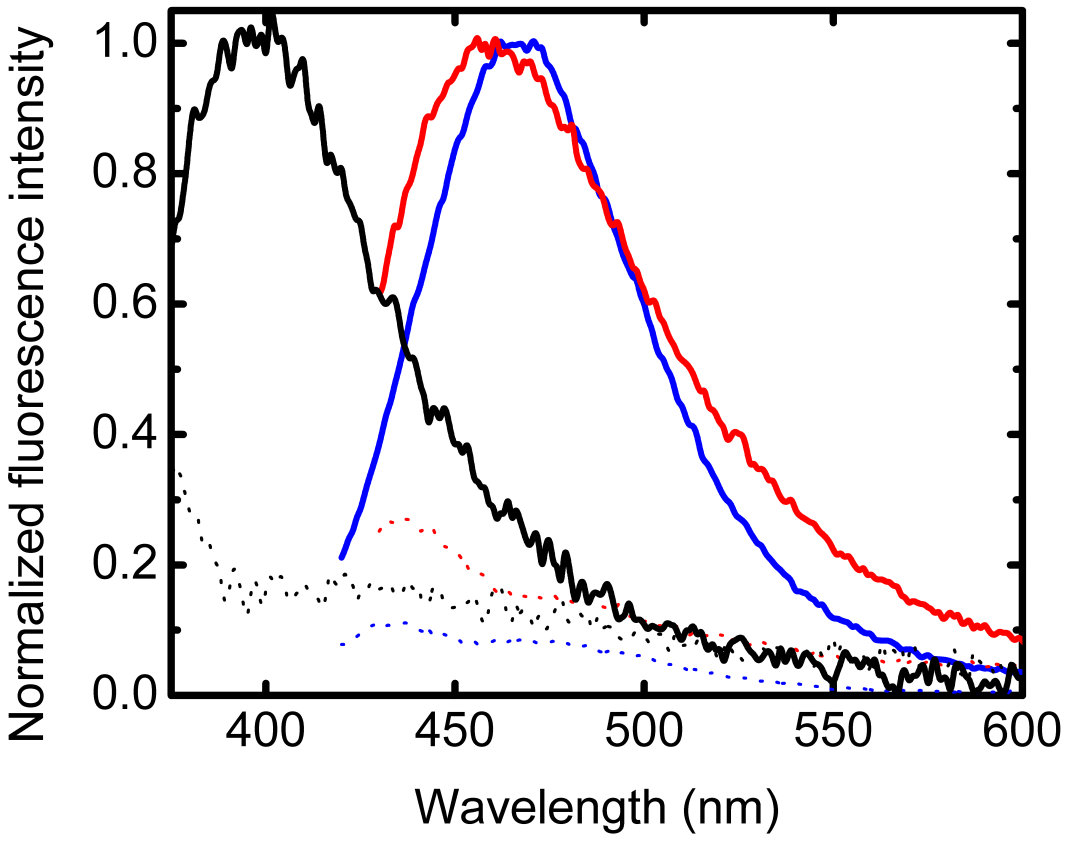


Figure S4 – Normalized fluorescence spectra for **1c** (black), **2a** (red) and **2b** (blue) (solid lines) and the corresponding blanks taken in the same conditions (dotted lines)

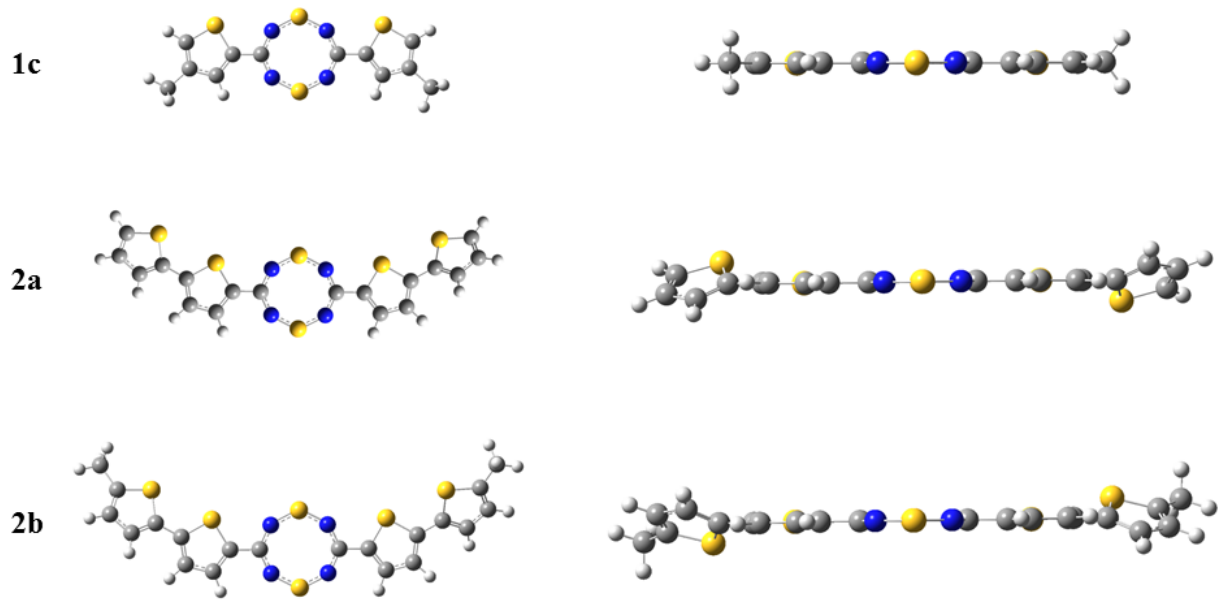
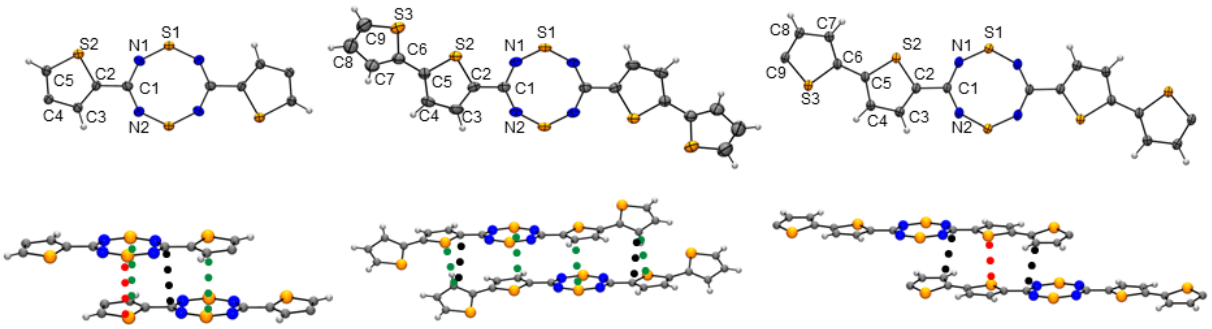


Figure S5. Top view (left) and side view (right) of geometry optimized structures of **1c** (top), **2a** (middle) and **2b** (bottom), where R = Me for **1c** and **2b**.



1c		**2a**		**2b**	
S1···C3'	3.482(4) Å	C7···S2'	3.44(2) Å	S2···S2'	3.568(6) Å
C1···C1'	3.429(6) Å	C3···S1'	3.424(6) Å	C7···C1'	3.415(2) Å
S1···S2'	3.613(2) Å	C7···C2'	3.44(2) Å	δ	3.50 Å
δ	3.46 Å	δ	3.53 Å	τ	21.7°
τ	39.3°	τ	38.7°		

Figure S6. Crystal structures of **1c**, **2a** and **2b** showing atom numbering and close intermolecular contacts along the π-stack. Hexyl chains are omitted for **1c** and **2b** for clarity. S···S' contacts are shown in red; S···C' contacts are shown in green; C···C' contacts are shown in black.

Density Functional Theory Calculations and Archival Files

Molecular geometry optimizations were performed on **1c**, **2a** and **2b** (where R = Me for **1c** and **2b**) at the DFT (B3LYP) level of theory with the 6-311+G(d,p) basis set, using the Gaussian 09W program package.[8] All geometries were fully optimized without symmetry constraints.

Archive file (geometry optimization) for **1c** (where R = Me):

```
#N B3LYP/6-311+G(d,p) OPT(EstmFC)\\b(4HT)8MR\\0,1\C,-0.6459505318,0
.,0.0164419628\C,-0.2990870749,0.,1.4836497848\C,1.0334515155,0.,1.988
6624869\C,1.1080436232,0.,3.3599524294\S,-0.4835333376,0.,4.069180112\
C,-1.2177595319,0.,2.5034476872\H,-2.2952939415,0.,2.4232700826\C,2.31
39013938,0.,4.2073368071\N,2.0823006634,0.,5.515838006\S,2.8172624751,
0.,6.9229148413\N,4.3893744327,0.,7.1474337807\C,5.5419644649,0.,6.486
3399606\N,5.7766155424,0.,5.1782200627\S,5.036055932,0.,3.7750851857\N
,3.4657984886,0.,3.5440343624\C,6.7484420126,0.,7.3340785606\C,8.06165
14906,0.,6.9380198649\C,8.98937799,0.,8.0227489145\C,8.3431702724,0.,9
.2311869814\S,6.6184478274,0.,9.0737167466\H,8.7873584701,0.,10.215987
0576\C,10.4835063353,0.,7.8488206714\H,10.99354731,0.,8.8139122582\H,1
0.8167022288,-0.8816495237,7.2925960341\H,10.8167022288,0.8816495237,7
.2925960341\H,8.3480509559,0.,5.8947333578\H,1.916245314,0.,1.36356041
88\H,0.2577595437,0.,-0.5959940488\H,-1.2316117791,-0.8823218117,-0.25
68057044\H,-1.2316117791,0.8823218117,-0.2568057044
```

Archive file (geometry optimization) for **2a**:

```
#N B3LYP/6-311+G(d,p) OPT(EstmFC)\\b(TT)8MR 2\\0,1\C,0.0141823577,-
0.0011990064,-0.0090184814\N,0.0152200674,-0.0005650727,1.3202177112\S
,0.9889133677,0.0005195002,2.5741808247\N,2.5753079208,0.0022666236,2.
5121800258\C,3.5932376983,0.0039657492,1.6573789231\N,3.5943223141,0.0
036970215,0.3275223793\S,2.6160734337,0.0022227614,-0.9205933785\N,1.0
312204499,0.0001284554,-0.8658440402\C,4.9275714449,0.0051390368,2.278
0419458\C,6.1545415847,0.0074599575,1.6593478921\C,7.2380832193,0.0266
004609,2.5683636097\C,6.8450102599,0.0299102015,3.8900849\S,5.09988253
63,0.0048446415,4.0145688431\C,7.6974938487,0.0244720655,5.0641752681\
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,6.4742717263\C,8.7109487028,0.3525294007,7.3273722722\S,7.2199546676,
0.7923312431,6.5654448195\H,8.8880262334,0.6257827816,8.3562171903\H,1
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3882617185\H,8.2764333111,0.0650371227,2.2668530919\H,6.2586125254,0.0
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519,-0.0034442597,0.3552125454\C,-5.2348371231,-0.0229643304,-0.957144
0372\C,-6.1396584069,0.524334603,-1.8385282494\C,-7.4941575567,0.33237
88018,-1.4522242709\C,-7.6190671725,-0.3525064651,-0.2762415975\S,-6.0
7607634,-0.7922262236,0.3740262838\H,-8.5203143178,-0.6265394792,0.250
261307\H,-8.3398561123,0.7000818662,-2.0181965283\H,-5.8360334582,1.07
22296687,-2.72061867\H,-3.4666844457,-0.0609997322,-3.200805911\H,-0.8
795302994,-0.0064589964,-2.7401321091
```

Archive file (geometry optimization) for **2b** (where R = Me):


```
#N B3LYP/6-311+G(d,p) OPT(EstmFC)\\b(HTT)8MR\\0,1\C,-0.2713123797,0
.5773402597,-0.0695116332\C,-0.0747331733,0.2044959106,1.3678294552\C,
0.9475401288,-0.5088906054,1.9324954262\C,0.813850601,-0.6956877982,3.
336040934\C,-0.3155939211,-0.1157327521,3.8617340296\S,-1.2285171814,0
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7.5812393227\C,-2.0418138391,-0.0715311293,7.3909212815\S,-2.436169047
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