

Supplementary Information for

Photophysical properties of 1,2,3,4,5-pentaaryl(cyclopentadienyl hydrotris(indazolyl)borate ruthenium(II) complexes

Sheng Gao,^a Yohan Gisbert,^b Seifallah Abid,^b Guillaume Erbland,^b Claire Kammerer,^b Alessandro Venturini,^a Gwénaël Rapenne,^{b,c*} Barbara Ventura,^{a*} Nicola Armaroli^a

^a Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche (CNR-ISOF), Via Gobetti 101, 40129 Bologna, Italy. E-mail: barbara.ventura@isof.cnr.it

^b CEMES, Université de Toulouse, CNRS, 29 rue Marvig, F-31055 Toulouse Cedex 4, France.

^c Division of Materials Science, Nara Institute of Science and Technology, NAIST, 8916-5 Takayama-cho, Ikoma, Nara 630-0192, Japan. E-mail: gwenael-rapenne@ms.naist.jp

Table of content

1. Photochemical stability tests in THF for molecular rotors **Ar₅L1-Ru-S1** and **L3-Ru-S1**, along with their related ligands/fragments **L1H**, **L2H**, **S1K**, **S1TI**, **L3Br** and **L3-Ru-(CO)₂Br** under ambient light at room temperature. (**Figure S1 page S2**)
2. Emission spectra of compounds **S1K** and **S1TI** in THF at 77 K acquired by using a pulsed source and a gated detection. (**Figure S2 page S3**)
3. Arbitrarily scaled absorption spectra (black line) and excitation spectra of compounds **L1H**, **L2H**, **L3Br**, **S1K** and **S1TI** in THF recorded at 298 K (green line) and 77 K (red line). (**Figure S3 page S3**)
4. Absorption spectra of the compounds **L3Br**, **L3-Ru-(CO)₂Br**, and **L3-Ru-S1** in THF solution at 298 K. (**Figure S4 page S4**)
5. Normalised absorption spectra (black line) and emission spectra of compounds **L3Br**, **L3-Ru-(CO)₂Br**, and **L3-Ru-S1** in air-equilibrated (green line) and deoxygenated (red line) THF both at 298 K and 77 K (blue line). The excitation wavelengths are 370 nm for **L3Br**, 360 nm for **L3-Ru-(CO)₂Br** and 350 nm for **L3-Ru-S1**. (**Figure S5 page S4**)
6. Emission maps for **L3-Ru-(CO)₂Br** in air-equilibrated (a and d) and deoxygenated (b and e) THF at 298 K and in frozen THF at 77 K (c and f). The maps are presented both as emission spectra distribution (left) and as contour plots (right). Excitation was moved from 300 nm to 395 nm with a 5 nm step. (**Figure S6 page S5**)
7. Absorption. HOMO-LUMO orbitals of the lowest electronic transition of **L1-Ru-S1**. (**Figure S7 page S6**)
8. Absorption. Couple of the HOMO-LUMO degenerate orbitals of the lowest electronic transition of **Ph₅L1**. (**Figure S8 page S6**)
9. Absorption. HOMO-LUMO orbitals of the lowest electronic transition of **L1**. (**Figure S9 page S7**)
10. Absorption. HOMO-LUMO orbitals of the lowest electronic transition of **L1H**. (**Figure S10 page S7**)
11. Absorption. HOMO-LUMO orbitals of the lowest electronic transition of **S1**. (**Figure S11 page S8**)
12. Overlap between calculated and x-ray structures of the two complexes. (A) overlap between part of the optimized **L1-Ru-S1** and x-ray structure and (B) overlap between calculated **Ph₅L1-Ru-S1** and **L1-Ru-S1** structures. (**Figure S12 page S8**)
13. DFT calculations of **L1**, **S1'**, **Ph₅L1**, **L1-Ru-S1'** and **Ph₅L1-Ru-S1'**. (**Tables page S9-S14**)
14. Experimental conditions and fitting results for the ns lifetime measurements of all the compounds. (**Tables S1 page S15-S18**)

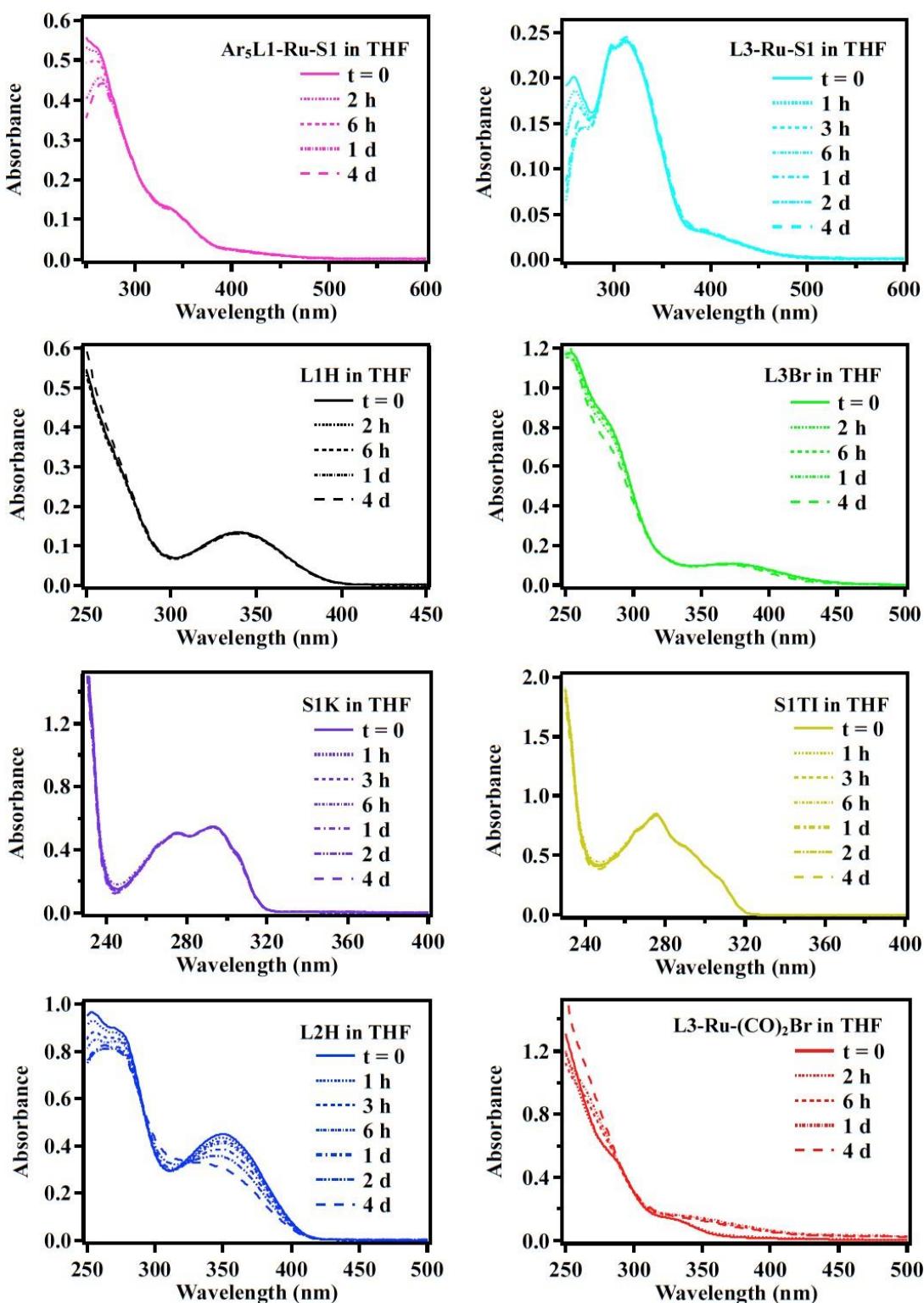


Figure S1. Photochemical stability tests in THF for molecular rotors **Ar₅L1-Ru-S1** and **L3-Ru-S1**, along with their related ligands/fragments **L1H**, **L2H**, **S1K**, **S1TI**, **L3Br** and **L3-Ru-(CO)₂Br** under ambient light at room temperature. The changes observed in the spectral region below 280 nm for Ar₅L1-Ru-S1 and L3-Ru-S1 are due to scattering artifacts caused by the presence of small amount of undissolved samples that is reducing over time.

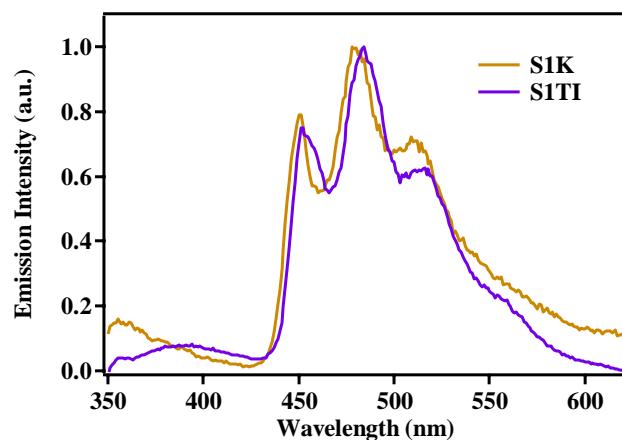


Figure S2. Emission spectra of compounds **S1K** and **S1TI** in THF at 77 K acquired by using a pulsed source and a gated detection.

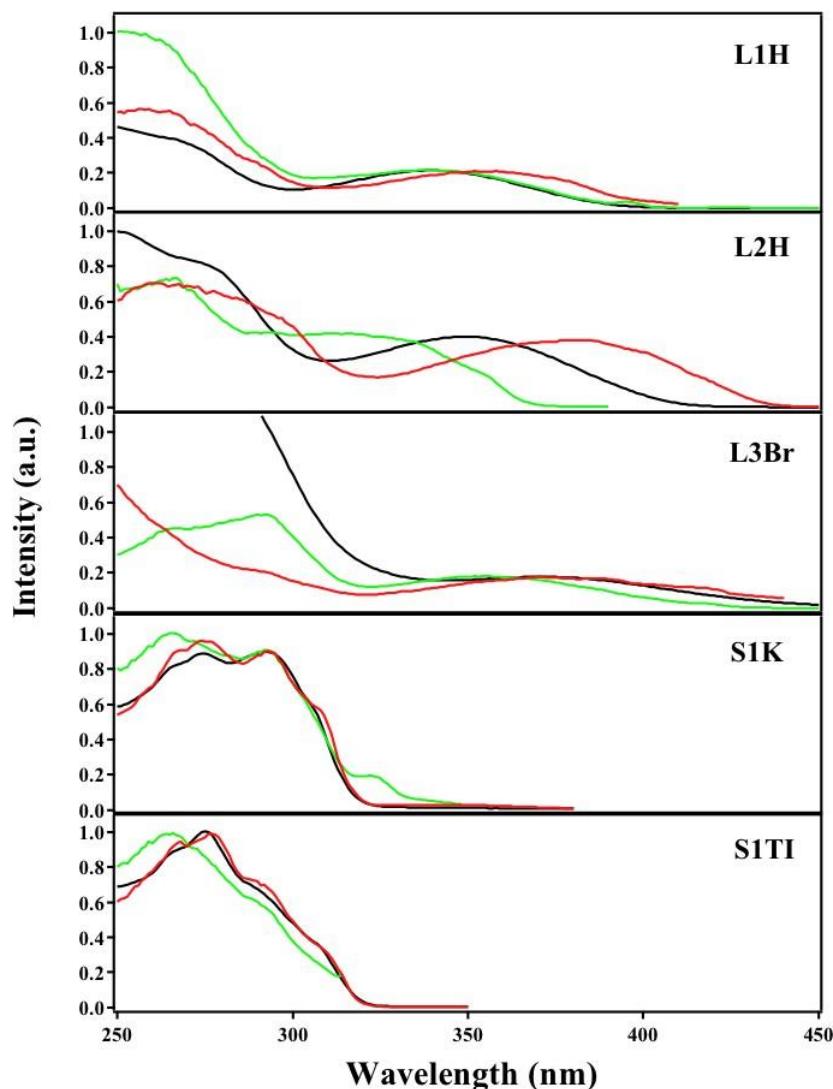


Figure S3. Arbitrarily scaled absorption spectra (black line) and excitation spectra of compounds **L1H**, **L2H**, **L3Br**, **S1K** and **S1TI** in THF recorded at 298 K (green line) and 77 K (red line).

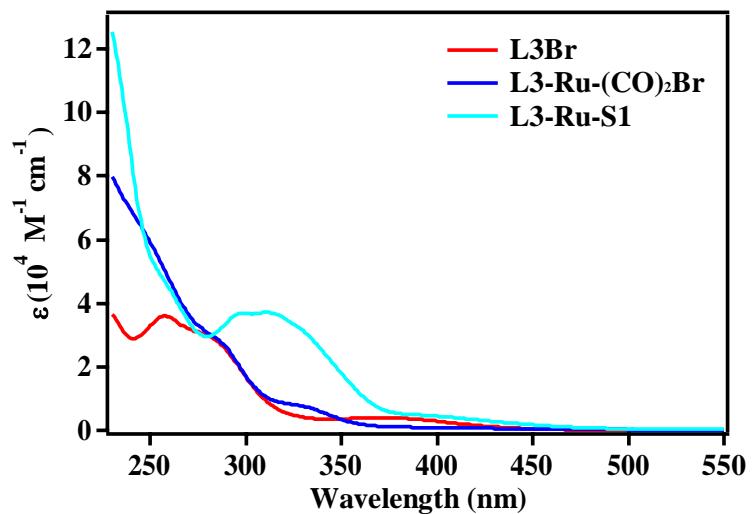


Figure S4. Absorption spectra of the compounds **L3Br**, **L3-Ru-(CO)₂Br**, and **L3-Ru-S1** in THF solution at 298 K.

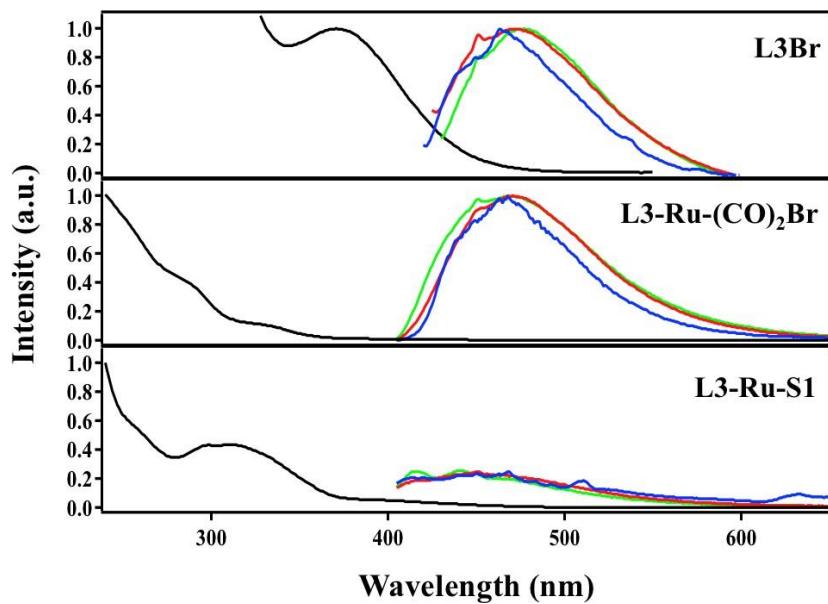


Figure S5. Normalised absorption spectra (black line) and emission spectra of compounds **L3Br**, **L3-Ru-(CO)₂Br** and **L3-Ru-S1** in air-equilibrated (green line) and deoxygenated (red line) THF both at 298 K and 77 K (blue line). The excitation wavelengths are 370 nm for **L3Br**, 360 nm for **L3-Ru-(CO)₂Br** and 350 nm for **L3-Ru-S1**.

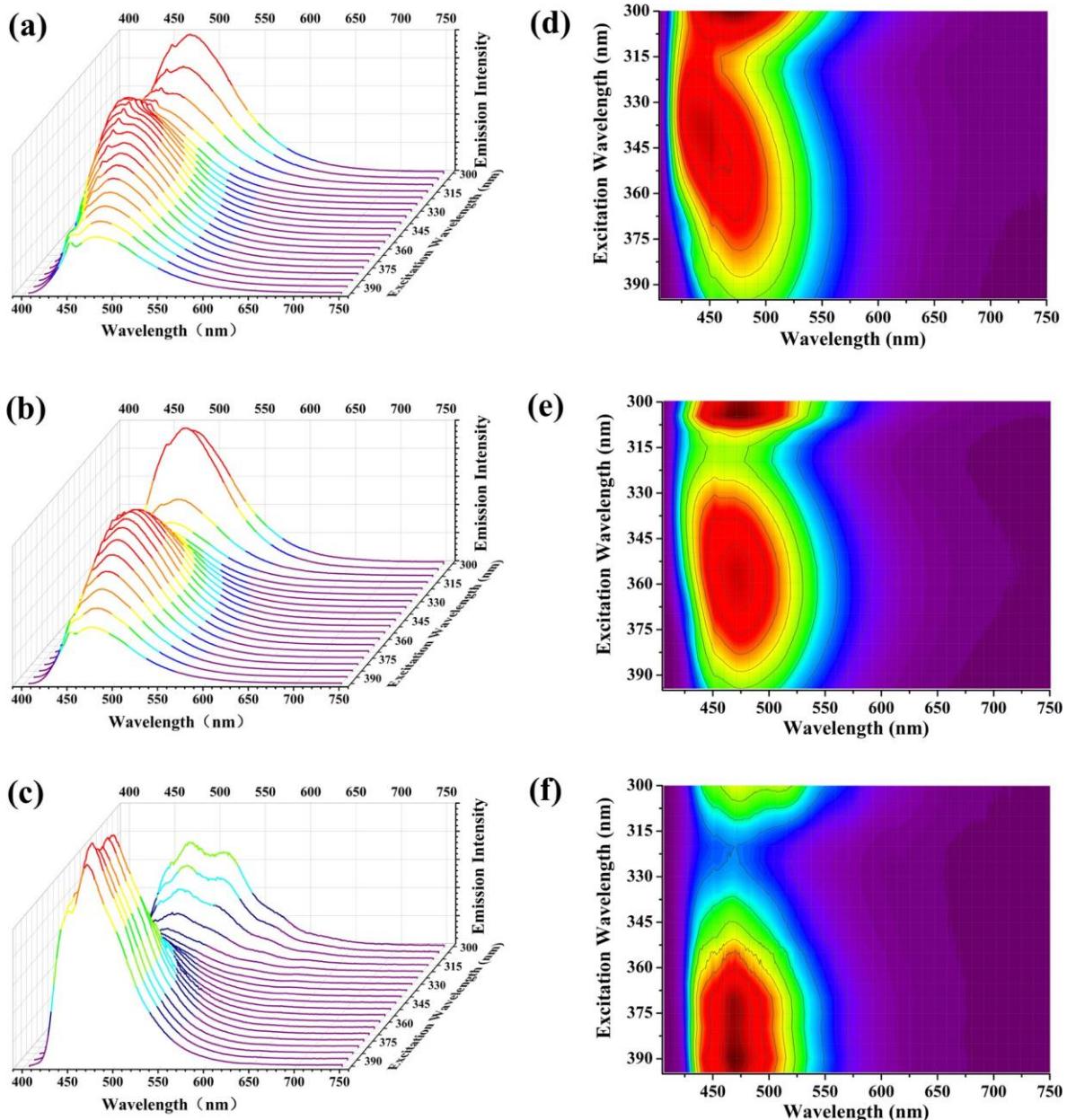


Figure S6. Emission maps for **L3-Ru-(CO)₂Br** in air-equilibrated (a and d) and deoxygenated (b and e) THF at 298 K and in frozen THF at 77 K (c and f). The maps are presented both as emission spectra distribution (left) and as contour plots (right). Excitation was moved from 300 nm to 395 nm with a 5 nm step.

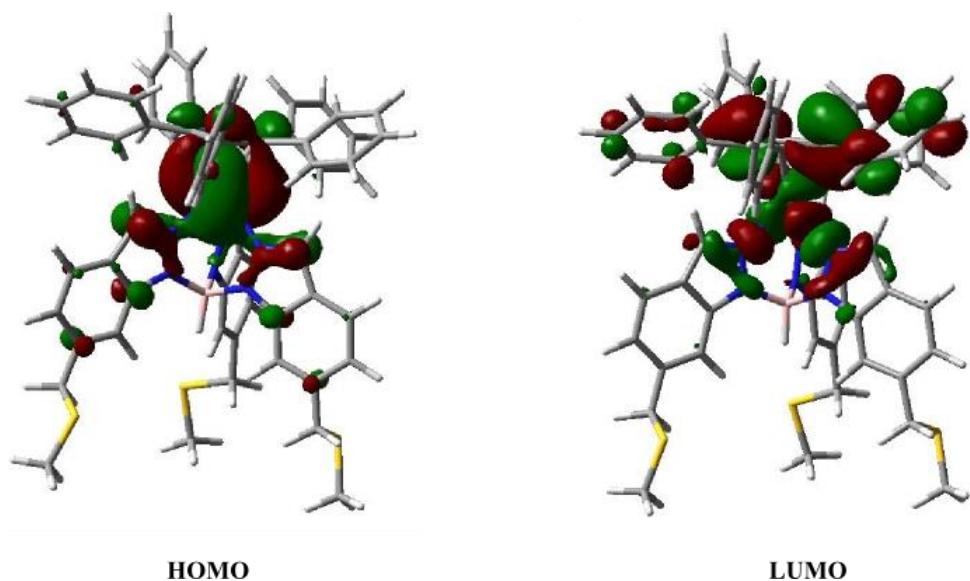


Figure S7. Absorption. HOMO-LUMO orbitals of the lowest electronic transition of **L1-Ru-S1'**.

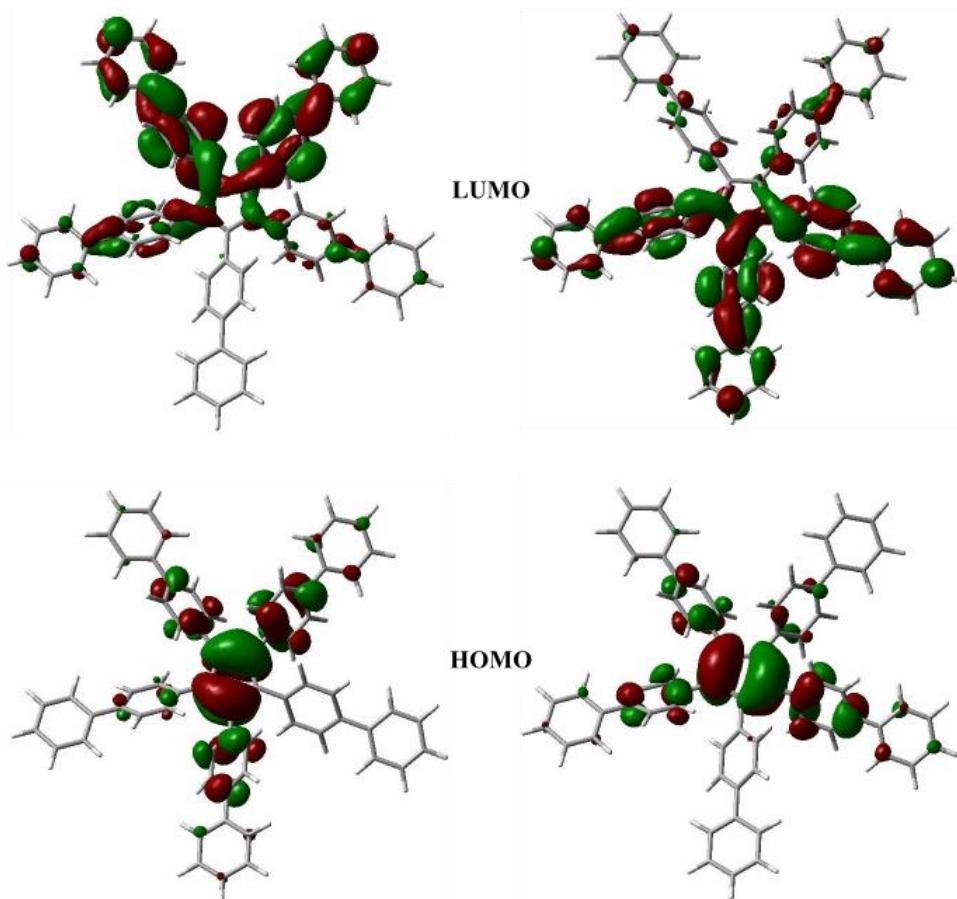


Figure S8. Absorption. Couple of the HOMO-LUMO degenerate orbitals of the lowest electronic transition of **Ph₅L1**.

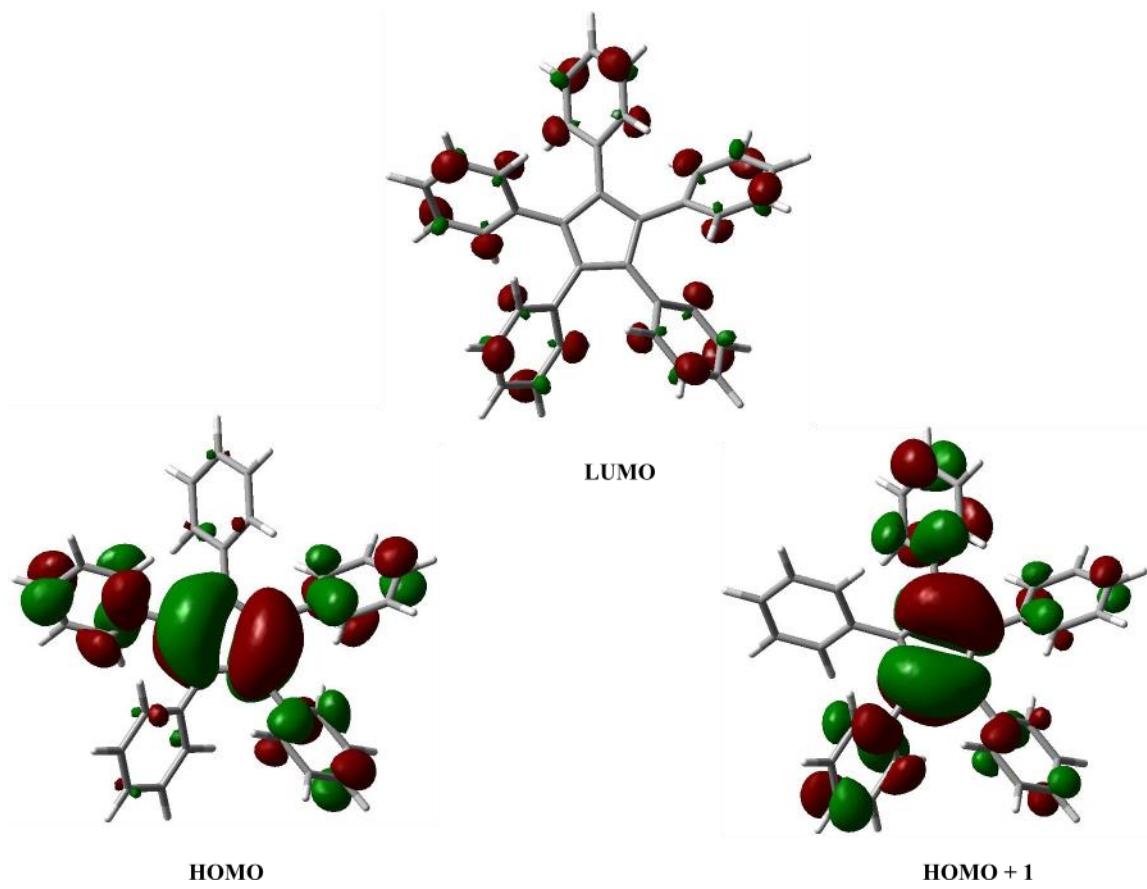


Figure S9. Absorption. HOMO, LUMO and HOMO+1 representing the two transitions to the same energy of **L1**.

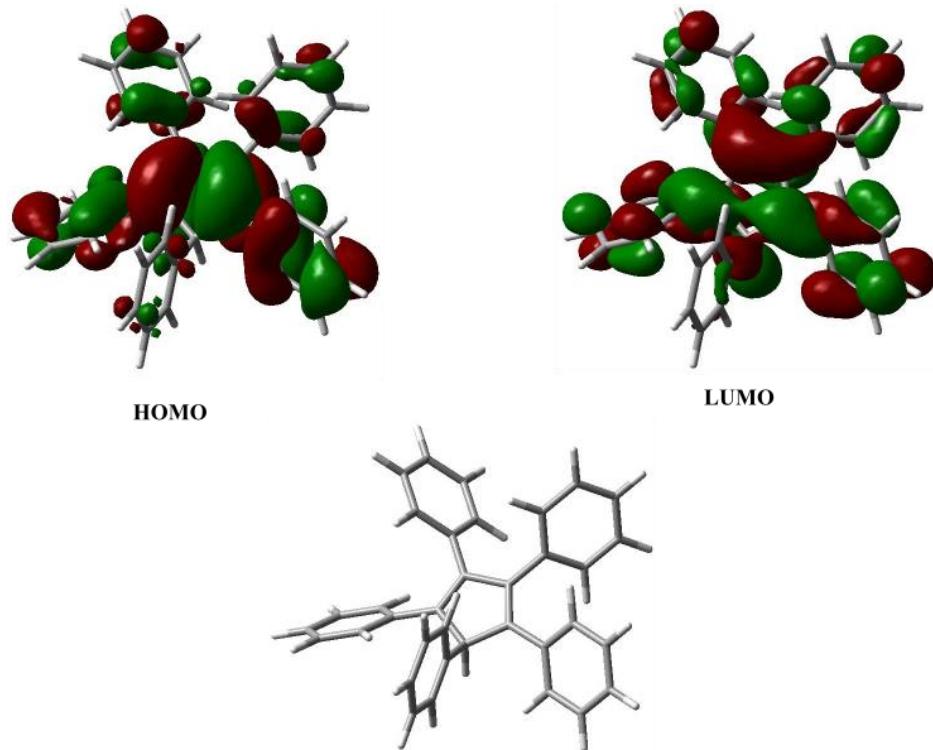


Figure S10. Absorption. Geometry and HOMO-LUMO orbitals of the lowest electronic transition of **L1H**.

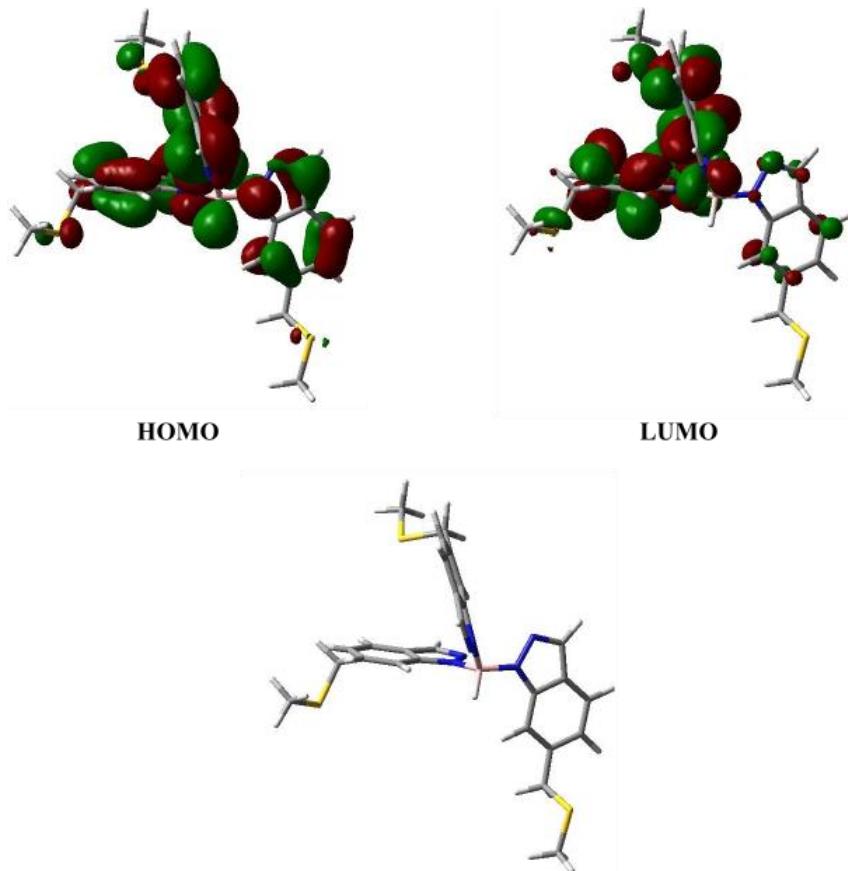


Figure S11. Absorption. Geometry and HOMO-LUMO orbitals of the lowest electronic transition of **S1'**.

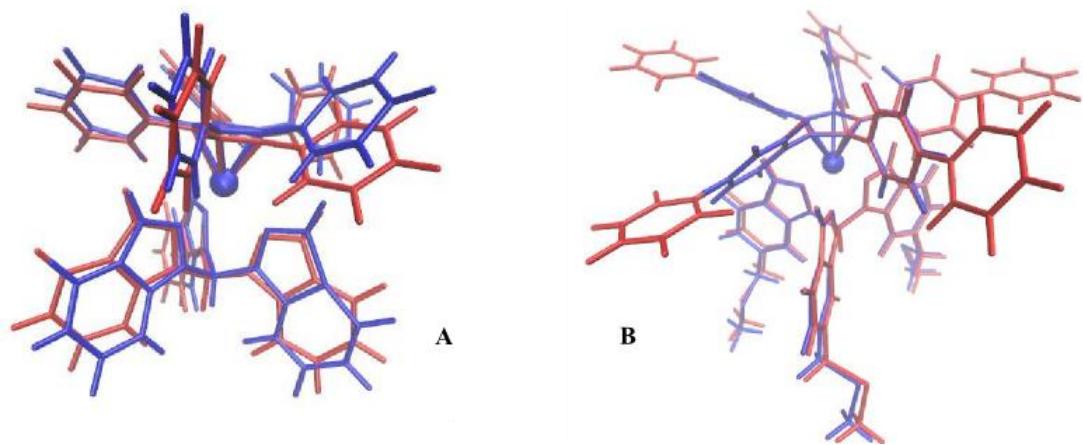


Figure S12. (A) Overlap between part of the calculated **L1-Ru-S1** (in red) and the corresponding X-ray structure of a parent compound (in blue) and (B) overlap between calculated **Ph₅L1-Ru-S1** (in red) and calculated **L1-Ru-S1** (in blue) structures.

XYZ optimised geometries

DFT M06 optimised energies

Basis set 6-31g(d,p) for C,N,O,H,S atoms

SDD for Ru atom

Implicit solvent SCRF=Tetrahydrofuran

L1H

E = -1348.374519

DG = -1347.940460

0 charge 1 molteplicity

C 0.58513400 0.97121900 -0.22403400

C 1.22637700 - 0.51178100
0.19219900

C 0.20427200 - -0.66108300
1.29239300

C - 0.7227190 -0.16387000
0.86819800 0

C - - -0.41186200
1.11174000 0.59107600

C - 1.7629360 0.11482800
1.87463100 0

C - 1.5683160 1.11454900
2.83394600 0

C - 2.9603810 -0.60983000
1.89378400 0

C - 2.5398260 1.37757600
3.79211100 0

H - 0.6429760 1.68771800
2.81910000 0

C - 3.9300240 -0.34955400
2.85502700 0

H - 3.1263060 -1.38724800
1.14976700 0

C - 3.7234590 0.64508400
3.80669300 0

H - 2.3732520 2.16002100
4.52880600 0

H - 4.8520390 -0.92619700
2.86024100 0

C - - -0.58601300

2.41765200 1.24706200

H 3.3053600 4.5066060 -1.51175300

0 0 - -0.72069600

H 6.4661590 0 1.31171700

H - 5.8806010 2.95400100 1.13236300

0

H - 4.48427300 0.85067100

4.5558550 0

H 0.1923790 0 - -1.70366100

C 0.4697550 0 1.65645300 - 0.24441600

0 2.4747300 0

C 0.5459020 0 - -0.26348500

0 3.7693750 0

C 0.6078460 0 - 1.62060300

0 2.2768370 0

C 0.7367220 0 - 0.58861100

0 4.8544870 0

H 0.4384630 0 - -1.33595300

0 3.92988500 - 2.47253100

C 0.7971480 0 3.3568930 0

H 0.5560970 0 - 2.01959300

0 1.26362600 - 1.95847900

C 0.8578580 0 4.6513180 0

H 0.7881010 0 - 0.17885900

0 5.86054800 - 3.54260400

H 0.8978980 0 3.19078200 -

H 1.0037490 0 2.62578300

0 5.49727500

L1

E = -1347.883500

DG = -1347.461989

-1

1

C - - -

0.98064600 0.70096500 0.00115800

C - 0.71825200 -

0.96897300 0.00149000

C	-	-	-1.40854500	C	0.38424900	1.14567800	-
	3.39055400	0.66004100					0.00121700
C	-	-	0.03420100	C	0.36545500		-
	2.72416700	2.46652900				1.15084400	0.00185400
C	-	-	-1.60302500	C	1.20909800		-
	4.62436700	1.26670300				0.00928800	0.00159200
H	-	0.2812540	-1.90540300	C	-	1.58932000	-
	3.16305300	0			2.15140100		0.00636000
C	-	-	-0.16093900	C	-	2.66328700	0.89040000
	3.96105500	3.07184400			2.27696600		
H	-	-	0.69056400	C	-	1.38145100	-
	1.99516100	2.93639000			3.20643000		0.91020500
C	-	-	-0.97985500	C	-	3.48888800	0.88125000
	4.91526000	2.47729100			3.39507500		
H	-	-	-2.24969000	H	-	2.84220300	1.6062730
	5.36041000	0.79447500			1.47605100		0
H	-	-	0.33590500	C	-	2.19853900	-
	4.18047900	4.01419100			4.33057700		0.91414400
C	2.66273300	-	-0.57747800	H	-	0.55991400	-
		0.46973600			3.13004600		1.62084700
C	3.57265300	0.1595210	0.28485200	C	-	3.26127200	-
		0			4.43267600		0.01965700
C	3.15674800	-	-1.47847700	H	-	4.31227900	1.5905500
		1.42342900			3.46119200		0
C	4.92726800	-	0.23075200	H	-	2.00962600	-
		0.13932500			5.13011200		1.62862500
H	3.20427000	0.8798900	1.01258300	H	-	3.90429600	-
		0			5.31026700		0.02449700
C	4.51295700	-	-1.53312400	C	-	-	0.0054510
		1.72076600			2.17714600	1.55283300	0
H	2.46885200	-	-2.15466100	C	-	-	-
		1.92841600			2.32240000	2.62234700	0.89339800
C	5.40502800	-	-0.68065100	C	-	-	0.9137390
		1.07806200			3.22555800	1.33121500	0
H	5.61438500	0.3567380	0.91244100	C	-	-	-
		0			3.45215800	3.43195000	0.88116700
H	4.87412100	-	-2.24569400	H	-	-2.81071000	-1.61329400
		2.45868900			1.52732200		
C	1.20223000	2.2922410	-0.00544400	C	-	-	0.9211170
		0			4.36112900	2.13228600	0
C	2.05384200	2.8483730	-0.96596100	H	-	-0.51211900	1.6254630
		0			3.13441400		0
C	0.94828500	3.0134320	1.16657100	C	-	-	0.0250720
		0			4.48218800	3.19172200	0
C	2.64654100	4.0874380	-0.75483500	H	-	-4.25256200	-1.59214300
		0			3.53307700		
H	2.24873800	2.2951780	-1.88295400	H	-	-1.93360000	1.6393860
		0			5.15486300		0
C	1.54522100	4.2505740	1.37970900	H	-	-3.82253400	0.0327190
		0			5.36857000		0
H	0.28075100	2.5930590	1.91716000	C	0.84904200	2.53866100	0.00203100
		0					
C	2.39621400	4.7912170	0.41996400	C	1.83112300	2.98009400	0.90415700
		0					
H	1.34424800	4.7950850	2.29932400	C	0.32962100	3.48604100	-
		0					0.89558600
H	2.86060100	5.7603200	0.58575800	C	2.27536300	4.29705600	0.90582900
		0					

H	2.2450450	2.26664100	1.61515700	H	-	-	-	
C	0.7639520	4.80630200	-0.88868900	C	1.66248500	2.73116800	1.58067100	
O	0			C	0.42584800	-	0.87092700	
H	-	3.16738000	-1.61012600		4.84911000			
	0.42779500			H	1.19886300	-	1.59861800	
C	1.7428250	5.22193400	0.01077900		2.98541700			
O	0			C	-	-	-	
H	3.0376060	4.60649800	1.61903400		0.42887800	5.50378700	0.02532900	
O	0			H	-	-	-	
H	0.3407990	5.51522200	-1.59848100		1.86921000	5.17972800	1.59708000	
O	0			H	1.03839900	-	1.55355600	
H	2.0865010	6.25417800	0.01418900		5.43686600			
O	0			C	2.46606000	-	0.02996700	
C	0.8077000	-	-0.00594500		1.01426900			
O	0	2.55135500		C	2.85123000	-	-0.84448300	
C	1.7821870	-	-0.90852600		2.04394100			
O	0	3.00856200		C	3.44467600	-	0.91988100	
C	0.2736040	-	0.89159100		0.54061300			
O	0	3.49062200		C	4.13417500	-	-0.82799800	
C	2.2050040	-	-0.91066800		2.56988700			
O	0	4.33254800		H	2.12387600	-	-	
H	2.2071660	-	-1.61989500		2.42362100	1.56011000		
O	0	2.30204000		C	4.73064900	-	0.93021300	
C	0.6867310	-	0.88465100		1.05849900			
O	0	4.81760000		H	3.17516900	0.24375700	1.62515000	
H	-	-	1.60602800		C	5.10692600	-	0.05760000
	0.47876100	3.16012600			2.08776900			
C	1.6584230	-	-0.01526900		H	4.40011600	-	-
O	0	5.24880300			3.34709000	1.54347400		
H	2.9617870	-	-1.62434100		H	5.45027800	-	1.65674000
O	0	4.65407500			0.68305400			
H	0.2527560	-	1.59477200		C	1.73361200	2.03456600	-
O	0	5.51960600				0.00230200		
H	1.9857570	-	-0.01883000		C	1.62066500	3.12486400	0.8762060
O	0	6.28634300				0		
C	2.6775800	-	0.00029900		C	2.81118900	2.05681300	-
O	0	0.02140500				0.90321200		
C	3.4010480	-	0.89841400		C	2.52833600	4.17341300	0.8535050
O	0	0.82354300				0		
C	3.4183120	0.76797200	-0.89498400		H	0.80736900	3.13335800	1.59999800
O	0				C	3.72501000	3.09907000	-
C	4.7907610	-	0.89868100			0.91983400		
O	0	0.84076000			H	2.91768500	1.23759800	-1.61213700
H	2.8501550	-	1.60803800		C	3.60522800	4.18472600	-
O	0	1.43906000				0.04244800		
C	4.8081870	0.76093300	-0.88959800		H	2.42193600	4.98505100	1.57225500
O	0				C	4.52925100	3.09079000	-1.65455200
H	2.8816790	1.39342200	-1.60671400					
O	0				C	-	2.28207600	0.01584200
C	5.5059230	-	0.00584400			1.40657700		
O	0	0.04609700			C	-	3.33207700	-0.87111200
H	5.3204840	-	1.60897500			1.11581900		
O	0	1.47346400			C	-	2.48412100	0.90805600
H	5.3516900	1.38444200	-1.59760200			2.47238300		
O	0				C	-	4.51124400	-0.86647100
H	6.5938410	-	0.00803200			1.84580600		
O	0	0.05546500			C	-	3.20393400	-
						0.30696900	1.58832800	
						-	3.65839900	0.90684800
						3.20934300		

Ph₅L1

E = -2502.317549

DG = -2501.525508

-1

1

C - 1.03381100 0.01154500
0.63742100
C 0.7774960 0.92289700 0.01372200
0
C 1.1096670 - 0.01762400
0 0.45738600
C - - 0.01284200
1.17984600 0.27829700
C - - 0.01784000
0.10021500 1.19961100
C - - 0.00909300
2.60522600 0.62237500
C - - 0.89786400
3.13493900 1.57276200
C - - -0.88393100
3.50671300 0.01971100
C - - 0.89217600
4.48155800 1.90303300
H - - 1.61519400
2.46800900 2.04797800
C - - -0.88369100
4.85534300 0.34185800
H - 0.70703900 -1.60048300
3.12735800
C - - 0.00337600
5.37612300 1.29312100
H - - 1.61872700
4.85655200 2.62282500
H - 0.12734700 -1.61295600
5.51462300
C - - 0.00970900
0.21528600 2.66148700
C - - -0.88601400
1.07030000 3.32443300
C 0.5262160 - 0.89026000
0 3.46593000
C - - -0.90124100
1.17731800 4.70675600

H - 1.70012800 1.62466000
2.71112300
C - 4.70192900 0.02015600
2.91363000
H - 3.78563900 1.63503600
4.00944900
H - 5.28776300 -
1.60783000 1.59235800
C 4.57489200 5.29630100 -
0.06143000
C 4.17625900 6.60854100 0.2264480
0
C 5.92417600 5.07262200 -
0.36693700
C 5.09000900 7.65528200 0.2118430
0
H 3.12851300 6.81206300 0.44029500
C 6.83797200 6.11926400 -
0.38714200
H 6.26375000 4.05790200 -0.56681600
C 6.42633800 7.41679000 -
0.09641700
H 4.75350400 8.66589600 0.43280400
H 7.88106700 5.91789900 -0.62128800
H 7.14147500 8.23582200 -0.10993900
C - 5.95170400 0.02159800
3.69769600
C - 7.18322600 -0.27582400
3.09854700
C - 5.94376100 0.32192600
5.06650000
C - 8.35954100 -0.27440300
3.83843500
H - 7.21924700 -
2.03119300 0.48634100
C - 7.11993900 0.32925500
5.80625900
H - 4.99631300 0.52911900
5.56077600
C - 8.33487100 0.02987400
5.19653700
H - 9.30342600 -
3.34791400 0.50225300
H - 7.08544300 0.56018600
6.86874500

H	-	9.2554320	0.03342800		C	-	-	-	
	5.77529900	0			C	2.13826200	1.09165300	2.89374600	
C	-	-	0.00242800		C	-	-	-	
	6.81066100	1.63719700			C	1.87662600	1.99355600	0.62477000	
C	-	-	-0.29479600		C	-	-	-	
	7.78401300	0.67373200			C	1.33925400	0.22242100	3.68204100	
C	-	-	0.29982200		C	-	-	-	
	7.24314000	2.93666500			C	3.37744500	1.74019200	3.02895700	
C	-	-	-0.29690000		C	-	-	-	
	9.13552400	0.99642100			C	3.10226500	2.61659300	0.77008800	
H	-	0.3492540	-0.50202600		H	-	-	0.2976030	
	7.47502600	0			H	1.30657900	2.09179100	0	
C	-	-	0.30322100		H	-	0.15116600	-	
	8.59471800	3.25934500			C	1.53124000		4.68232500	
H	-	-	0.50678000		C	-	-	-	
	6.50507200	3.70956700			C	3.84768700	2.48472300	1.96875800	
C	-	-	0.00362500		H	-	-	-	
	9.54892100	2.29113800			C	3.95722300	1.64964000	3.94534400	
H	-	-	-0.52452500		H	-	-	-	
	9.87136600	0.22821500			C	4.81187800	2.98759500	2.03810400	
H	-	-	0.53133700		C	-	0.87474500	0.85000900	
	8.90380500	4.27710100			C	0.96540500		-	
H	-	-2.54370200	0.00426700		C	-	0.65186600	2.17718300	
	10.6065760				C	1.39646300		-	
	0				C	-	1.80083500	0.01204400	
C	-	-	-0.04962900		C	1.60760900		-	
	0.53379800	6.97531300			C	-	-	2.64461700	
C	-	-	-1.24967500		C	0.51383600	0.35606100	-	
	0.75962500	7.66309800			C	-	1.37716900	2.68792500	
C	-	-	1.12482800		C	2.48617500		-	
	0.40888800	7.72976300			C	-	2.49976700	0.52850700	
C	-	-	-1.27480800		C	2.68347700		-	
	0.85875300	9.04874600			H	-	1.95097800	-	
H	-	-	-2.17962900		H	1.28188400		1.01723000	
	0.83340400	7.10218700			H	-	-	3.6209090	
C	-	-	1.10042400		C	0.48129500	0.82757600	0	
	0.50331200	9.11586500			C	-	2.28843400	1.86483200	
H	-	-	2.07383500		C	3.11113700		-	
	0.25960800	7.21787300			H	-	1.21823400	3.70641100	
C	-	-	-0.09969800		H	2.83436800		-	
	0.72982600	9.78366100			H	-	2.86439600	2.23172600	
H	-	-	-2.22087400		C	3.96024900		-	
	1.02775200	9.55846300			N	1.8460060		-	
H	-	-	2.02733600			0	1.27198500	0.63108500	
	0.40901700	9.67744100			N	-	-	-	
H	-	-	-0.11908500			0.26664000	0.47014000	1.82038600	
	0.80534000	10.8682250			N	0.0842390	0.03930100	0.60596700	
	0					0	-	-	
C	6.47415200	-2.64173500	0.06935200		N	1.5116540		-	
	C	6.70848000	-3.99468700	-0.21094700			0	2.58135200	0.75931300
	C	7.57978600	-1.83052700	0.35849900		N	0.3513810		-1.70763800
	C	7.99673200	-4.51541400	-0.20556600			0	0.70769900	-
	H	5.8637230	-	-0.41188800		N	-	0.14251300	-
		0	4.65110800			0.24709400		3.03519200	
	C	8.86802700	-2.35130100	0.36975200			-	-	0.37962300
	H	7.4263130	-	0.55214500			3.67994000	3.38137800	
		0	0.77039500			H	-	-	0.0399570
	C	9.08410900	-3.69681500	0.08613200			4.37907300	4.15622400	0
						H	-	-	0.9796560
							2.89506500	3.85824400	0
						C	6.02292300	0.9636420	0.97856500
							0	-	-

H 8.1509490 -0.42066200
 0 5.57056200
 H 9.7098320 0.59128800
 0 1.69882600
 H 10.0921970 -4.10441800 0.09247700
 0

S1' [With methyl groups instead of ethyl in S1]

E = -2592.806614

DG = -2592.371810

-1
 1
 H 1.3678940 0.87970300 -1.09133200
 0
 B 0.81009600 -0.14790500 -0.76274100
 C 3.11624500 -1.15770700 -0.14972000
 C 3.63432600 -2.46230300 0.01348300
 C 3.87576000 -0.02190000 0.16842300
 C 2.55948500 -3.29629300 -0.39210100
 C 4.94339200 -2.63949600 0.49090500
 C 5.16026400 -0.21344400 0.64509200
 H 3.4654640 0.97948300 0.04898800
 0
 H 2.5233570 -0.43294400
 0 4.37970000
 C 5.68802400 -1.52115600 0.79757700
 H 5.3593700 -0.62146700
 0 3.63643300
 H 6.7061570 -1.17130400
 0 1.62699200
 C - -1.69697600
 1.39871100 1.22480400

H 5.42254200 1.87230000 1.10801300
 H 6.59584400 0.79252600 1.89961700
 C - 3.51350100 -0.31246400
 3.39454800
 H - 3.34165100 -
 3.21309600 1.38029900
 H - 3.49082800 -
 4.47799700 0.13632100
 S -2.79525000 5.1994990 0.11092100
 0
 S 7.22816300 1.2557950 -
 0 0.37912000
 S -4.59974800 - 1.46685200
 2.21824700
 C - 6.15206400 -1.00251000
 3.86870700
 H - 7.21001000 -
 3.63068400 0.86904200
 H - 5.87717600 -
 3.68843700 2.04655700
 H - 5.99193400 -
 4.92381900 0.75851600
 C 8.12221400 2.6556550 0.35611600
 0
 H 8.89947300 2.96048400 -0.34860900
 H 7.44851200 3.50106800 0.52809700
 H 8.59345500 2.36470700 1.30048000
 C - - 2.68301900
 5.21778500 3.41825200
 H - - 3.1835790
 4.38740800 3.92646500 0
 H - - 3.4290880
 5.79629200 2.86818900 0
 H - - 2.2068590
 5.86723100 4.15996600 0

L1-Ru-S1'

E = -4035.381491

DG = -4034.492357

0

1

C - - - 2.37217700
 2.08370100 0.53914500
 C - - - 3.27252600
 1.24644500 1.23356100
 C - - - 4.40574200
 1.79710100 1.85945100
 C - - - 4.59401500
 3.15815200 1.78026800
 C - - - 3.68552200
 3.99703800 1.08257000
 C - - - 2.56779200
 3.47093600 0.46210200
 C 0.04354600 -
 1.11114800
 H - - - 5.10980000
 1.16474500 2.39480500
 H - - - 5.45596500
 3.61873800 2.26108300
 H - 0.0623400 1.86434600
 4.11532000 0
 H 2.6407050 0.14168100 3.51273900
 0
 N - - - 1.58668400
 0.00826400 0.40530300
 R 1.49922600 - -0.00255400
 0.06478400
 N 0.3752210 1.77804500 -0.30849000
 0
 C 0.78178300 3.03065000 -0.48191900
 C - 3.02793400 -0.53753700
 1.44831500
 C - 3.88546800 -0.64009000
 0.33042900
 H 1.8363470 3.27584300 -0.49404200
 0
 C - 3.51586900 -0.64254500
 2.76015500
 C - 5.26340100 -0.85538700
 0.51624800
 C - 4.87085000 -0.86024000
 2.92591800
 H - 2.8535960 -0.56084300
 3.61967900 0
 C - 5.73601400 -0.95933200
 1.80392100
 H 0.3361060 5.93312900 -0.94028100
 0
 H - 6.7973710 -1.12392900
 1.98481400 0
 N - - - -1.12153100
 0.12040300 1.06579700
 C - - - -1.79969700
 0.12133100 2.20737900
 C - - - -1.59923600
 2.23891700 1.53614800
 C - - - -2.14661300
 1.44258300 2.56692100

H -6.21113300 - -
 2.13371300 1.68737400
 H -6.06061900 - -
 3.74911000 2.42006900
 S -6.20564500 - -
 2.02970600 4.10647900
 S -4.77713400 6.15283700 0.6777590
 S -6.21823000 - 3.14426400
 2.56186700
 C - 6.83335900 0.21107900
 6.39498200
 H -6.82681200 7.29735300 1.10103600
 H -6.28728800 7.59351400 -
 0.56922900
 H -7.06530700 6.04100600 -
 0.13681700
 C - - -
 7.99077200 2.34396400 3.99281200
 H -8.44941600 - -
 1.97941800 4.91504900
 H -8.19218800 - -
 3.41548700 3.89517000
 H -8.42694500 - -
 1.80852100 3.14356200
 C - - - 3.65545200
 7.94052800 2.29573800
 H -8.32628000 - 3.24980500
 1.35505700
 H -8.53412200 - 3.25862400
 3.12277000
 H -8.02618100 - 4.74669700
 2.28872500
 C 3.84583200 1.57223100 1.7340720
 0
 C 2.95339900 2.53209800 2.2157120
 0
 C 5.15200000 1.55306800 2.2374790
 0
 C 3.36003000 3.45907100 3.1719120
 0
 H 1.9274560 2.52944600 1.85015500
 0
 C 5.55808300 2.47607500 3.1938300
 0
 H 5.8481650 0.79730600 1.87346000
 0
 C 4.66170000 3.43397500 3.6628050
 0
 H 2.6520130 4.19766000 3.54107500
 0
 H 6.5754110 2.44586300 3.57728800
 0
 H 4.9766650 4.15525800 4.41326400
 0
 C 3.51983600 - 2.36232800
 1.45917500
 C 4.22055100 - 2.45295700
 2.66958400
 C 3.17209800 - 3.55396700
 0.80665300
 C 4.53913800 - 3.68859700
 3.22098000

H	0.8047020	-	-2.00299100	H	4.5301090	-	1.54304700
	0	2.73266300			0	3.17848200	
C	-	-	-1.68617600	C	3.48665200	-	4.78924200
	3.63943700	1.56354100			1.36103300		
C	-	-	-2.82460100	H	0.9845150	-	3.07112900
	2.04912200	3.64012200			0	1.50564700	
C	-	-	-2.33801900	C	4.16837100	-	4.86239800
	4.22083700	2.63506700			2.57240400		
H	-	-	-1.24391300	H	5.0850720	-	3.73167100
	4.25084300	0.77882900			0	4.16050700	
C	-	-	-2.91523000	H	3.1978290	-	5.69896900
	3.42196100	3.65763400			0	0.83993700	
H	-	-	-3.25562900	H	4.4151550	-	5.82922800
	1.44843900	4.43742500			0	3.00460000	
H	-	-	-3.43033100	C	2.81158700	-	-
	3.92482300	4.47504000				3.01232300	0.35446800
C	3.44799900	0.54889200	0.73893500	C	1.83361900	-	0.42055100
						3.65219500	
C	3.28028700	-	1.03370000	C	3.53363400	-	-
		0.85777100				3.77669400	1.27713700
C	3.06139100	-	-0.20140700	C	1.58451300	-	0.27499500
		1.56329700				5.00961100	
C	3.41948500	0.69587200	-0.70253300	H	1.2451580	-	1.12193200
					0	3.06232700	
C	3.16589100	-	-1.28311900	C	3.27552600	-	-
		0.59199200				5.13702300	1.43081100
N	-	-	-1.01241200	H	4.3033150	-	-
	1.40738100	0.63132500			0	3.30305700	1.88199000
N	-	1.7625920	-0.34056800	C	2.30136000	-	-
	0.98537100	0				5.75803100	0.65724900
N	-	-	1.37715900	H	0.8160070	-	0.88128500
	1.30385600	0.03312400			0	5.48364500	
B	-	0.48172300	-0.00719300	H	3.8444190	-	-
	1.74879600				0	5.71187000	2.15809600
H	-	0.6965400	-0.01123400	H	2.0988650	-	-
	2.93179300	0			0	6.81946300	0.77946200
C	-	5.45249800	-0.95308500	C	3.31136600	-	-
	4.30195100					0.88218900	2.73183300
H	-	6.2628360	-1.69245900	C	2.25477800	-	-
	4.34167200	0				0.89390400	3.64274700
H	-	4.6904220	-1.23309500	C	4.60977500	-	-
	5.03929100	0				1.10673200	3.20740200
C	-	-	3.91699100	C	2.48632000	-	-
	5.47570300	1.06918200				1.14801600	4.99243700
H	-	-	4.98844100	H	1.2475400	-	-
	5.71211300	1.08719800			0	0.68340100	3.29080200
H	-	-	3.47262400	C	4.84269700	-	-
	5.94174200	0.18121100				1.36037400	4.55357100
C	-	-	-2.47388100	H	5.4417630	-	-
	5.70948100	2.71062900			0	1.07853900	2.50321400

C	3.77741100	-	-5.45079000	H	4.0187380	-	3.54275900
		1.38677800		0	1.44867400		
H	1.65087400	-	-5.68886900	C	6.19844300	-1.59392000	0.89754000
		1.15119400					
H	5.85782200	-	-4.90376900	H	5.7426770	-	-
		1.53260600		0	1.26848600	1.17726100	
H	3.95569900	-	-6.50518900	H	7.2559900	-	0.72223100
		1.58424200		0	1.78664500		
C	3.70829600	1.92281100	-1.47179100	C	-	0.64662700	-1.32777600
				2.07063000			
C	2.98418500	2.25148600	-2.62664700	C	-	1.52541300	-1.77960400
				1.01261300			
C	4.73463200	2.78400100	-1.06528500	C	0.03372900	0.72240500	-2.35580200
C	3.27145600	3.40515000	-3.34386200	C	-	-	-
				1.71174600	0.70203200	1.71842400	
H	2.16481900	1.6115000	-2.94311800	C	-	-	-
		0		0.41403600	0.66531200	2.33068900	
C	5.01859600	3.94274900	-1.78187200	N	2.1947840	-	1.42255500
				0	0.85889400		
H	5.31808100	2.5444390	-0.17976700	N	-	-	2.4672450
		0		0.04609200	1.33019000	0	
C	4.28731200	4.25949500	-2.92165600	N	0.9007260	0.98375600	2.45297000
				0			
H	2.68950500	3.6442730	-4.23091600	B	1.24403000	-0.51495400	2.58151500
		0					
H	5.81885700	4.5980380	-1.44577900	H	1.7784480	-	3.63722200
		0		0	0.73074500		
H	4.50683900	5.1670860	-3.47903900	C	-	-	6.68799500
		0		0.66695200	3.93671300		

Ph₅L1-Ru-S1'

E = -5189.77363392

DG = -5188.514972

0 1

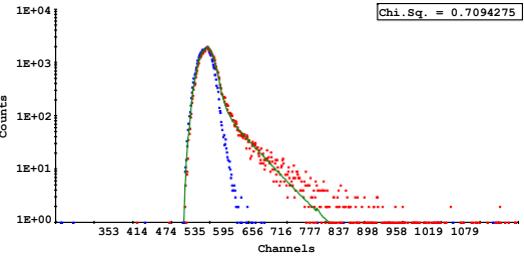
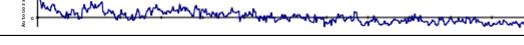
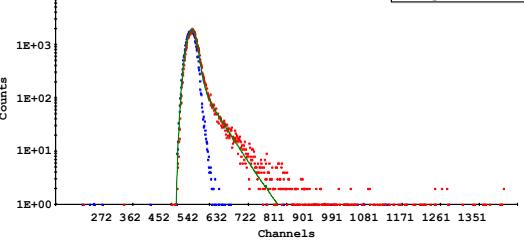
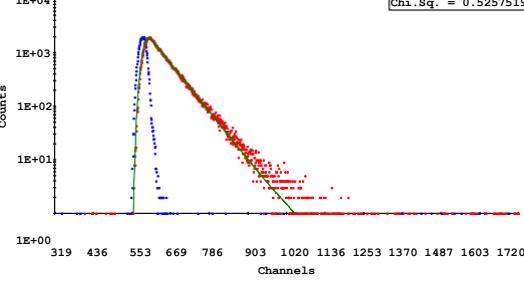
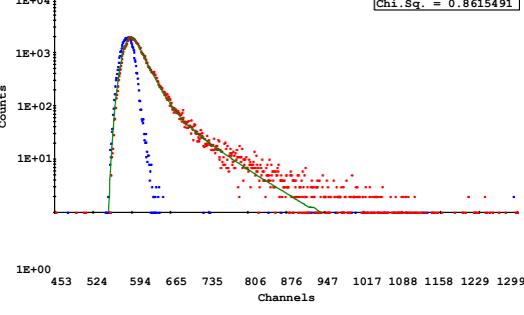
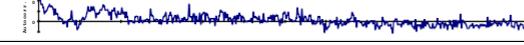
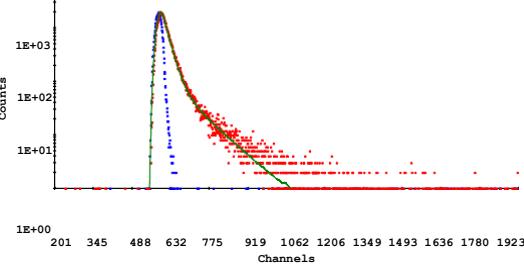
C	1.30463100	2.02413600	3.23314100	S	6.67801700	-1.96624400	3.33684100
C	0.98619500	3.22339700	2.55897200	H	6.2993360	-	4.30839500
C	1.28831900	4.46506600	3.14770900		0	1.62649600	
C	1.89773900	4.46695900	4.38100300	H	7.6573320	-	3.16388800
C	2.21538900	3.25919800	5.05759000		0	1.50154100	
C	1.92986900	2.03165800	4.48998300	S	6.92306500	-	3.40799100
C	0.39696200	2.79503700	1.34912200		3.78574500		
H	1.04567100	5.3959860	2.64104300	S	-1.46200400	-2.90014400	7.97994100
		0		S	4.70718800	3.58023900	6.11762200
H	2.14898100	5.4098850	4.86478900	C	-	-	9.44174900
		0		0.85910000	3.79338500		
H	2.18029100	1.1056020	5.00399900	H	-	-	10.3248550
		0		1.25287700	3.28464300	0	
H	-	3.2364090	0.00873100	H	-	-	9.4397120
		2.22928900	0	1.21493100	4.82859600	0	

N	0.35215600	1.4698370	1.30285000	H	4.9794340	2.79107300	8.40145600
		0			0		
R	-	0.0723360	-0.30025100	H	6.2963950	3.86552600	7.87335800
	0.24238600	0			0		
N	-0.86105800	-	1.38945200	H	4.7266750	4.56167000	8.34198100
		1.16517800			0		
C	-	-	1.60290100	C	-	1.10548000	-0.80317800
	1.97767800	1.85213600			3.37712100		
C	-	-	3.37753300	C	-	1.00414500	0.54767600
	0.65672100	2.13784600			3.71504000		
C	-	-	2.85193900	C	-	1.70126600	-1.67464300
	1.91536000	2.50588800			4.29608000		
H	-	-	0.86927000	C	-	1.47472600	1.01167000
	2.77366500	1.86191900			4.93745000		
C	-	-	4.63090200	H	-	0.5799240	1.24253800
	0.22234600	2.59678400			2.99153600	0	
C	-	-	3.58360500	C	-	2.17294200	-1.21098300
	2.76472500	3.35592500			5.51548900		
C	-	-	5.33514700	H	-	1.7912990	-
	1.06578800	3.43564800			4.04411000	0	2.73129700
H	0.74630600	-	5.03524200	C	-	2.06689800	0.14276700
		2.30965800			5.86092200		
C	-	-	4.80971000	H	-	1.4118140	2.07429900
	2.33264800	3.80539500			5.16520300	0	
H	-	-	3.18584600	C	-	2.99728900	-1.83093700
	3.73253700	3.65174800			1.12166200		
H	-	-	5.40400000	C	-	3.69119800	-2.94232900
	2.96433100	4.46424600			0.62358600		
N	1.80692700	-	0.14095300	C	-	3.73807900	-0.86435300
		0.60758500			1.81774400		
C	2.86761600	-	-0.64822100	C	-	5.06260900	-3.06784900
		0.72851400			0.78872900		
C	3.52991300	-	1.44448300	H	-	3.1441140	-
		1.12652900			0.11883600	0	3.73494700
C	4.00578600	-	0.11545500	C	-	5.11072700	-0.98790400
		1.06764500			1.97563500		
H	2.78609900	-	-1.71693700	H	0.0168750	3.38959100	0.52862300
		0.56876800			0		
C	4.38661600	-	2.51908000	C	-	5.80416600	-2.09027800
		1.41213700			1.46209600		
C	5.36409000	-	-0.15880000	H	-	5.5628960	-
		1.31092600			0.41463400	0	3.95904200
C	5.72072500	-	2.23448700	H	-	5.6575980	-
		1.63662100			2.48981400	0	0.19987500

C	1.31843400	1.2077240	-2.89901500		C	-7.23295700	-	-0.78881400
	0					6.3913390		0
C	2.12056400	2.0923710	-2.16375900		H	-6.79272400	-	-
	0					4.30034200	0.56673400	
C	1.78412300	0.7876300	-4.14900200		C	-6.75051200	-	-1.15814000
	0					7.6440200		0
C	3.34018400	2.5285910	-2.65427900		H	-5.05980200	-	-
	0					8.73966200	1.92066900	
H	1.79361800	2.4041700	-1.17264000		H	-8.24972500	-	-
	0					6.28616300	0.41711800	
C	3.01322000	1.2180450	-4.63528300		H	-7.38989400	-	-
	0					8.52049300	1.08442300	
H	1.17710100	0.1181420	-4.75363200		C	-1.63215500	7.2645210	-2.22208100
	0					0		
C	3.81799100	2.0924630	-3.89834700		C	-2.79371900	7.8972470	-1.76151400
	0					0		
H	3.95607000	3.1857600	-2.04301300		C	-0.63525000	8.0516730	-2.81220300
	0					0		
H	3.34020400	0.8879280	-5.61964200		C	-2.95312400	9.2722130	-1.88679000
	0					0		
C	0.18852700	-	-3.05533800		H	-3.59141900	7.2998800	-1.32335200
	1.81139500					0		
C	1.07885100	-	-2.48279600		C	-0.79449100	9.4265890	-2.93808500
	2.72024100					0		
C	-	-	-4.38282500		H	0.28592200	7.5821550	-3.15294100
	0.20484000	2.02115400				0		
C	1.58075300	-	-3.21948700		C	-1.95421200	10.0427480	-
	3.78622200					0	2.47576000	
H	1.36021200	-	-1.43883500		H	-3.86622200	9.7431600	-1.52985900
	2.60310100					0		
C	0.29748800	-	-5.11988000		H	-0.00478800	10.0208730	-3.39210700
	3.08387200					0		
H	-	-	-4.84133100		H	-2.07893500	11.1185070	-2.57383800
	0.91122800	1.32873100				0		
C	1.20759000	-	-4.55284200		H	-6.22272600	2.6114690	-1.91265500
	3.98525600					0		
H	2.25214300	-	-2.73882300		C	-7.15922300	2.5674580	0.63800900
	4.49544000					0		
H	-	-	-6.15842500		C	-7.84532500	1.8931390	1.65573300
	0.00463800	3.20574200				0		
C	-	-	-1.61996800		C	-7.73593700	3.7254450	0.10146700
	2.56384700	1.90250000				0		
C	-	-	-1.28213000		C	-9.06852900	2.3606510	2.12156100
	2.03955800	3.15820600				0		
C	-	-	-1.88084800		H	-7.42526600	0.9774200	2.06830600
	3.93691100	1.81928900				0		
C	-	-	-1.19856600		C	-8.95936600	4.1931950	0.56669600
	2.85424400	4.27591500				0		
H	-	-	-1.03667900		H	-7.20579300	4.2784250	-0.67222500
	0.98511800	3.24987600				0		
C	-	-	-1.79387000		C	-9.63107400	3.5125760	1.57856100
	4.75239000	2.93996800				0		
H	-	-	-2.16745100		H	-9.58883400	1.8174590	2.90721300
	4.37416600	0.86621500				0		
C	-	-	-1.44784900		H	-9.38629900	5.0990310	0.14211000
	4.23018500	4.19078000				0		
H	-	-	-0.89640300		H	-	3.87845800	1.9424960
	2.42065800	5.22737400				0		
H	-	-	-2.02745900					
	5.81123800	2.84537800						
C	5.12970600	2.5358600	-4.41078100					

	0	
C	5.93281200	1.6717070 -5.16580600
	0	
C	5.60351700	3.8286230 -4.15400300
	0	
C	7.16761900	2.0866490 -5.64994600
	0	
H	5.59494300	0.6538790 -5.35306700
	0	
C	6.83894900	4.2438210 -4.63695400
	0	
H	4.98424800	4.5234260 -3.58924000
	0	
C	7.62622400	3.3748170 -5.38751500
	0	
H	7.77902300	1.3970060 -6.22755700
	0	
H	7.18490000	5.2545260 -4.43241100
	0	
H	8.59277400	3.6995210 -5.76544100
	0	
C	1.75088500	- 5.33336900
	5.11534300	
C	3.06855600	- 5.14086600
	5.54887600	
C	0.96388200	- 6.28165900
	5.78069200	
C	3.58243100	- 5.87093400
	6.61398000	
H	3.70414600	- 4.42672800
	5.02815100	
C	1.47757700	- 7.01276200
	6.84542000	
H	- -	-6.42793400
	0.07093100	5.47577300
C	2.78893300	- 6.81024100
	7.26694800	
H	4.61072500	- 5.71097600
	6.93023600	
H	0.84702200	- 7.73837500
	7.35424600	
H	3.19052500	- 7.38171700
	8.10038400	
C	- -	-1.34783600
	5.09868700	5.38041300
C	- -	-1.71622400
	4.62643100	6.64642600
C	- -	-0.88239800
	6.41520600	5.27143800
C	- -	-1.62215900
	5.44361200	7.76674400
H	- -	-2.10452800
	3.61455300	6.74825100

Table S1. Experimental conditions and fitting results for the ns lifetime measurements of all the compounds.

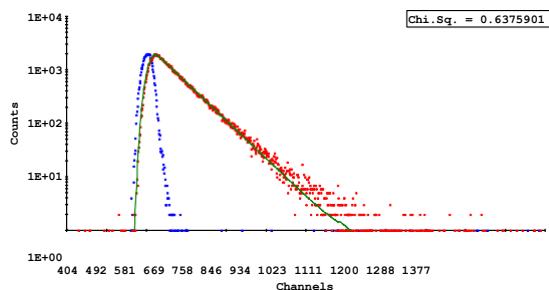
Compounds	Conditions	Decays (top) and residual distributions (bottom)	Model	τ (weighted amplitudes)
Air-equibrated THF at 298K		 	2	$\tau_1 = 0.2$ ns (not considered) $\tau_2 = 1.9$ ns
L1 H	Deoxygenated THF at 298 K	 	2	$\tau_1 = 0.2$ ns (not considered) $\tau_2 = 1.9$ ns
	THF at 77 K	 	1	3.1 ns
L2 H	Air-equibrated THF at 298K	 	2	$\tau_1 = 1.0$ ns (85%) $\tau_2 = 3.5$ ns (15%)
	Deoxygenated THF at 298 K	 	2	$\tau_1 = 1.2$ ns (86%) $\tau_2 = 5.2$ ns (14%)

L2H
K

THF at 77

1

3.0 ns

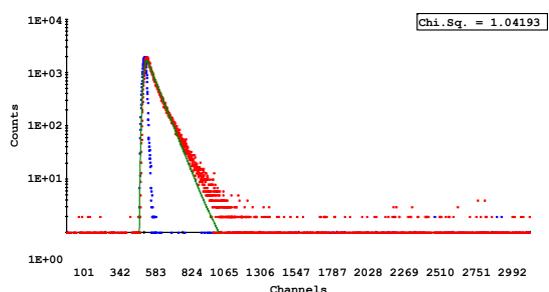


L3Br
K

THF at 77

1

3.2 ns

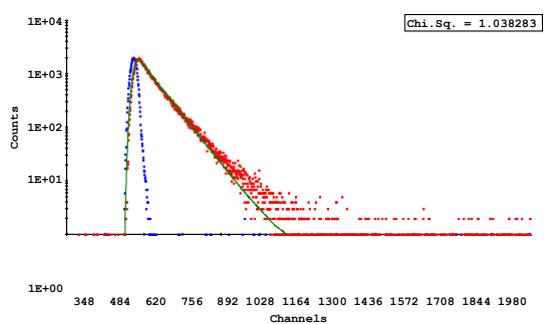


L3-
Ru-
(CO)₂
Br

THF at 77
K

1

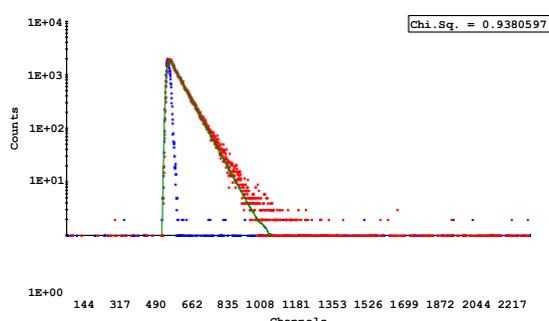
3.5 ns



Air-
equilibrated
THF at
298K

1

3.0 ns

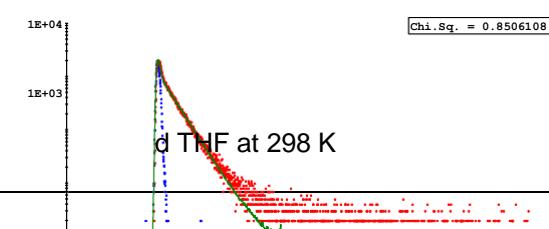


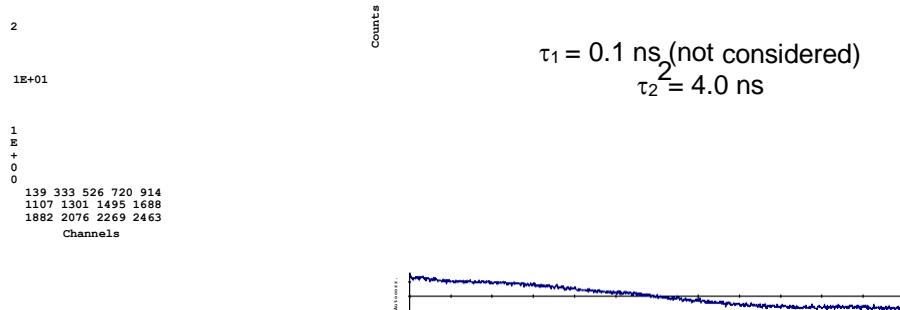
S1
K

Deoxygenate

d THF at 298 K

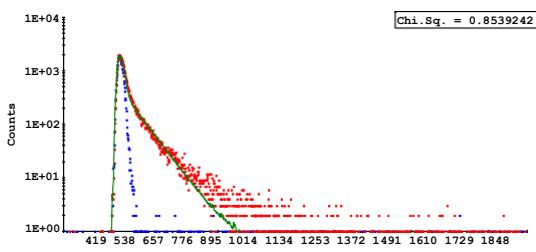
1
E
+
0





S1K
K

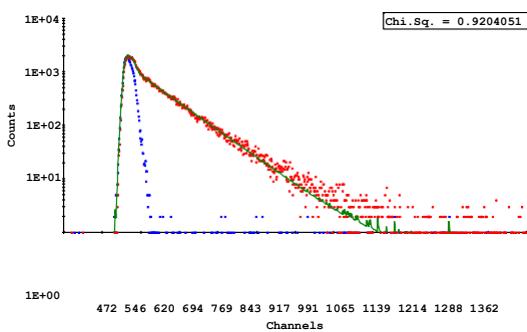
THF at 77
K



2

$$\begin{aligned}\tau_1 &= 0.2 \text{ ns} \\ &\text{(not considered)} \\ \tau_2 &= 3.0 \text{ ns}\end{aligned}$$

Air-equibrated
THF at
298K

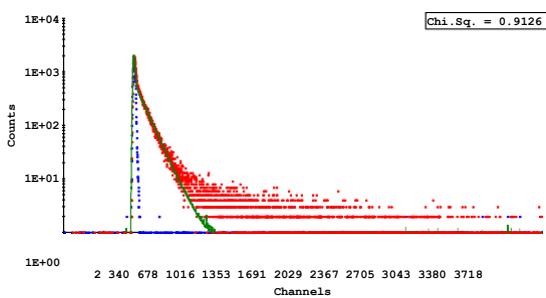


2

$$\begin{aligned}\tau_1 &= 0.1 \text{ ns} \text{ (not considered)} \\ \tau_2 &= 3.5 \text{ ns}\end{aligned}$$

S1
TI

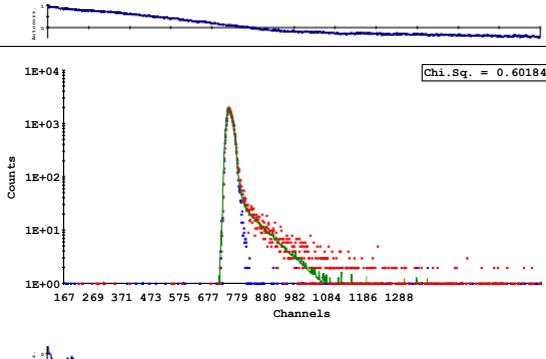
Deoxygenated
THF at
298 K



2

$$\begin{aligned}\tau_1 &= 0.1 \text{ ns} \text{ (not considered)} \\ \tau_2 &= 4.9 \text{ ns}\end{aligned}$$

THF at 77
K

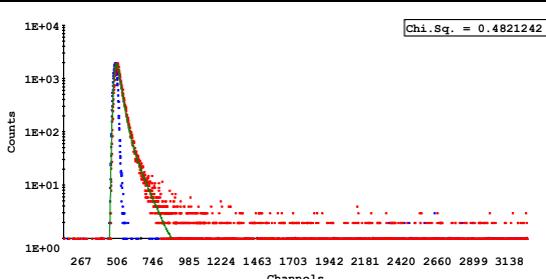


2

$$\begin{aligned}\tau_1 &= 0.1 \text{ ns} \text{ (not considered)} \\ \tau_2 &= 3.3 \text{ ns}\end{aligned}$$

Ar₅L1-Ru-S1
equibrated

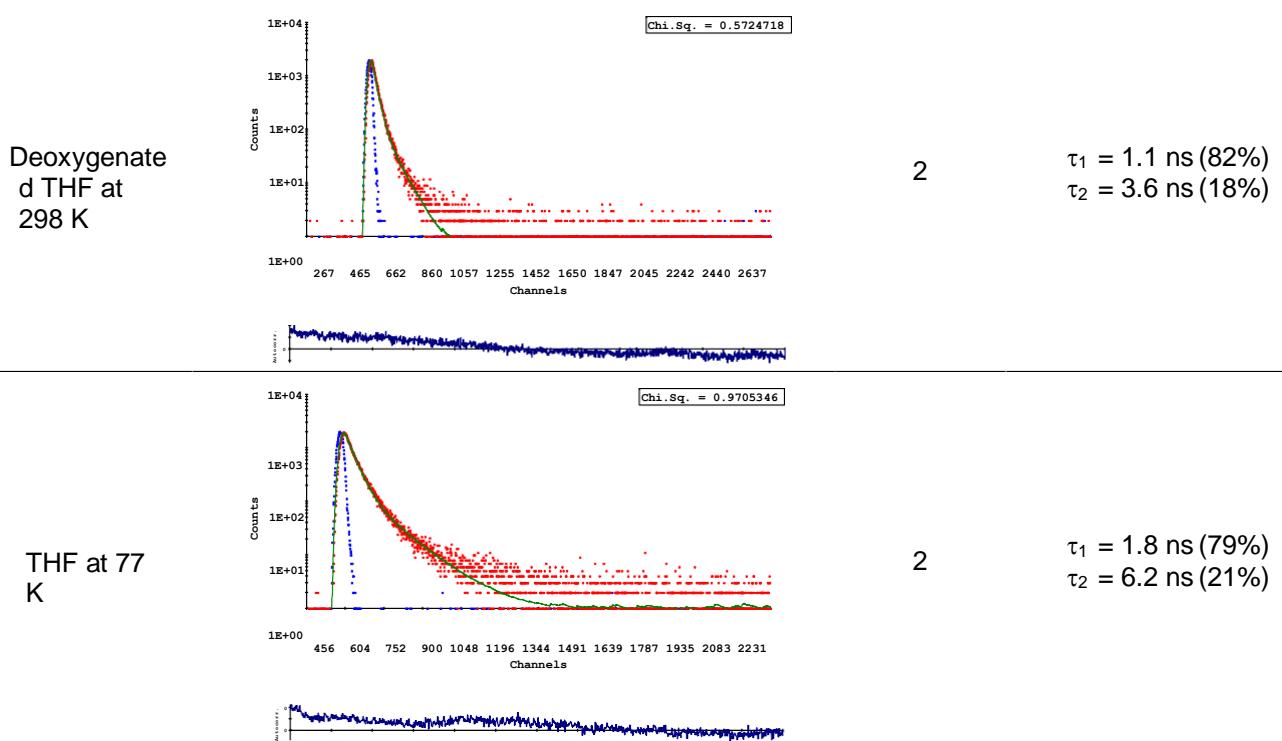
Air-equibrated
THF at



2

$$\begin{aligned}\tau_1 &= 1.1 \text{ ns (82\%)} \\ \tau_2 &= 3.2 \text{ ns (18\%)}\end{aligned}$$





Red dots indicate the luminescence decays of the samples; blue dots represent the pulse profile of the excitation source; the green lines indicate the fittings.

Fitting function model 1: $I(t) = I_0 + I_1 * e^{-t/\tau_1} (-t/\tau_1)$

Fitting function model 2: $I(t) = I_0 + I_0 * e^{-t/\tau_0} (-t/\tau_0) + I_1 * e^{-t/\tau_1} (-t/\tau_1)$

For model 2, the weighted amplitudes are expressed as: $\beta_3 = I_3 \tau_3 / \sum I_i \tau_i$
