

SUPPLEMENTARY INFORMATION

Stabilization of dichalcogenide ligands in the coordination sphere of ruthenium system

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I Experimental Details.

I.1 Spectroscopic Details

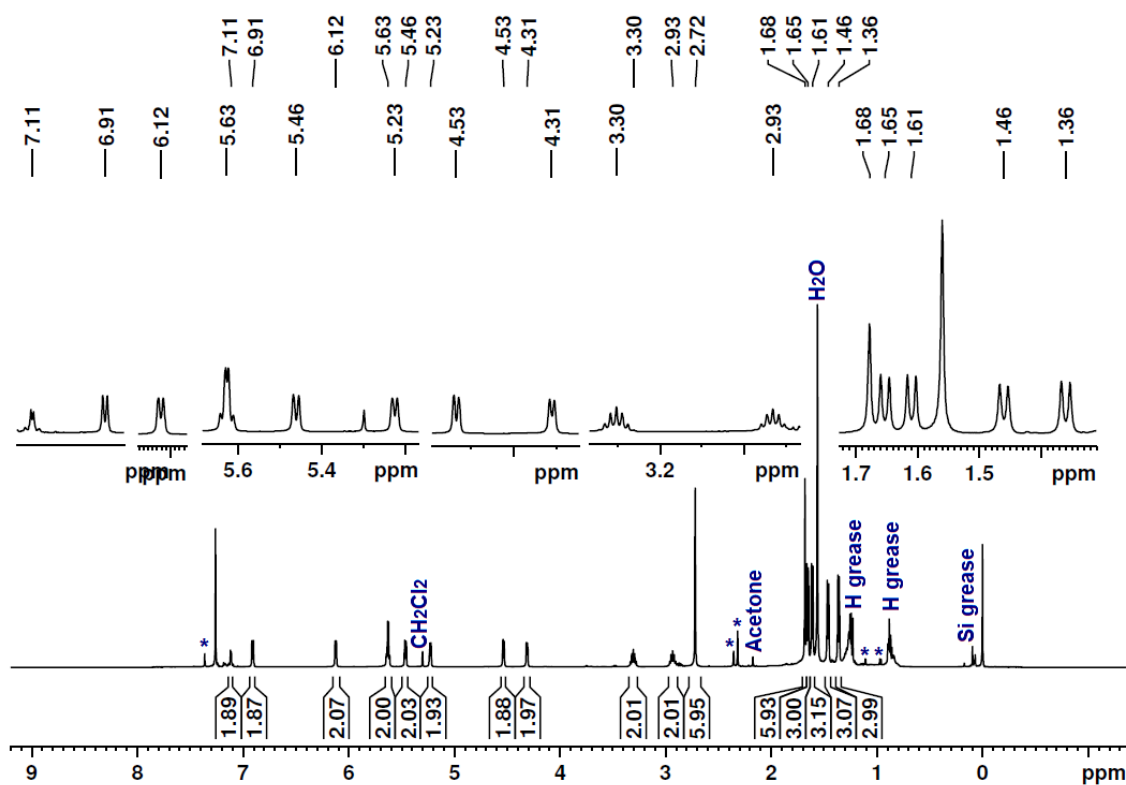


Fig. S1. ¹H NMR spectrum of **1** in CDCl₃. (* = Inseparable impurity)

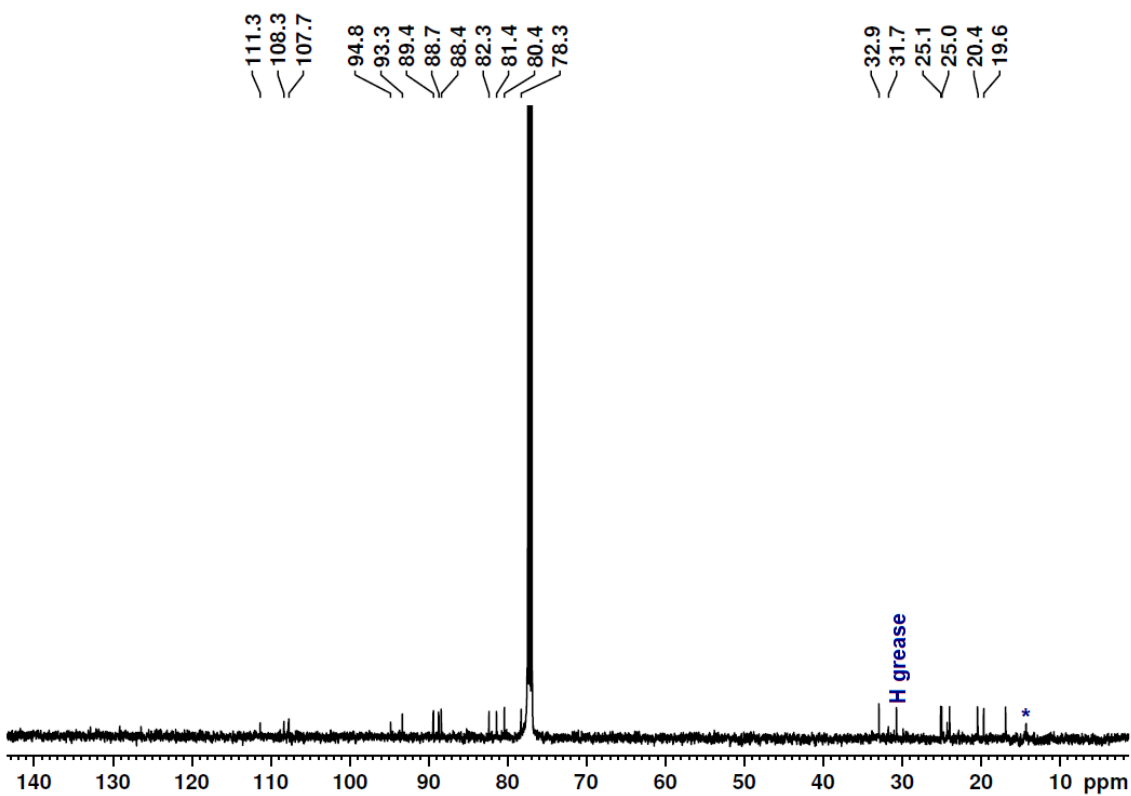


Fig. S2. ¹³C{¹H} NMR spectrum of **1** in CDCl₃. (* = Inseparable impurity)

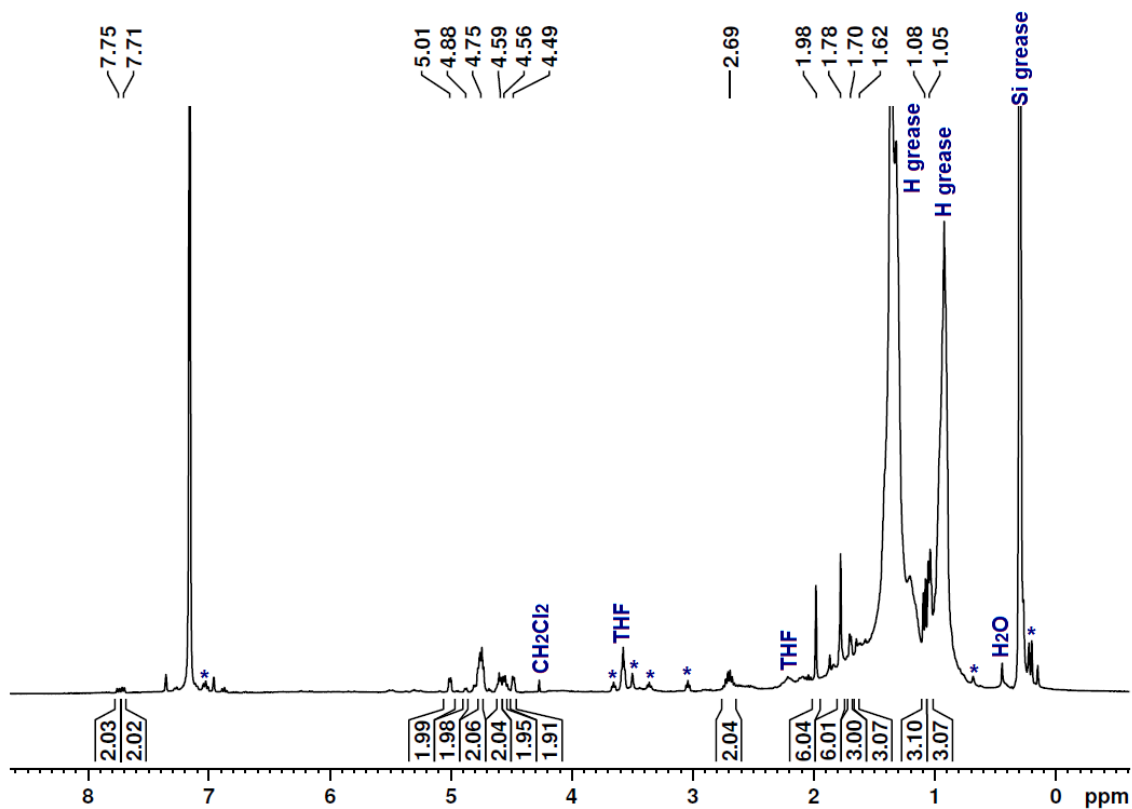


Fig. S3. ¹H NMR spectrum of **2** in C₆D₆. (* = Inseparable impurity)

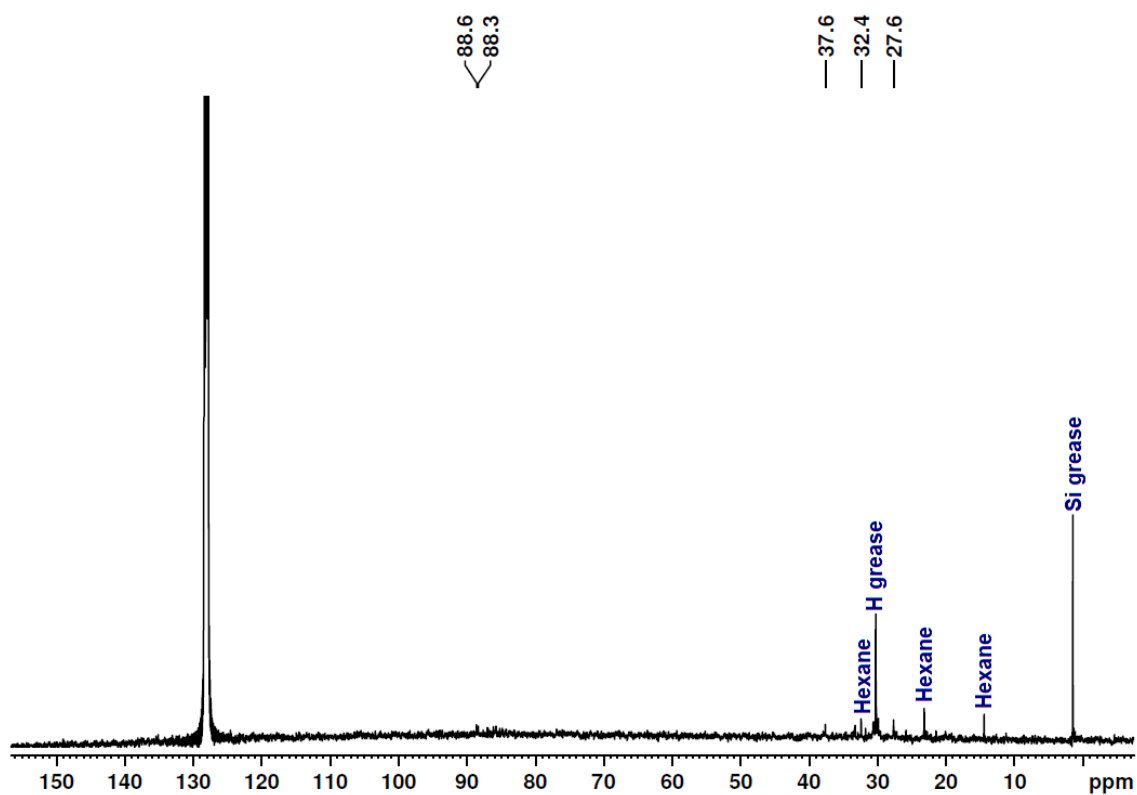


Fig. S4. ¹³C{¹H} NMR spectrum of **2** in C₆D₆.

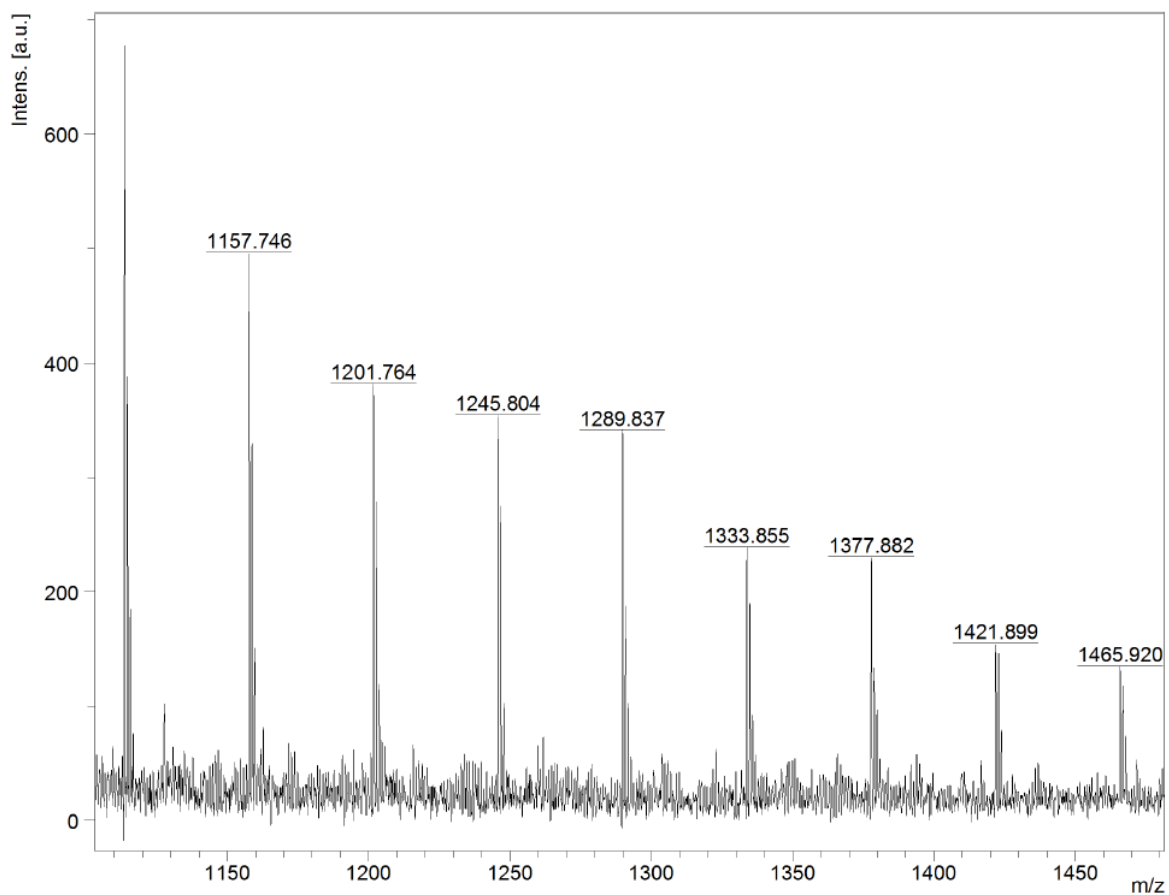


Fig. S5. MALDI-TOF spectrum of **2**.

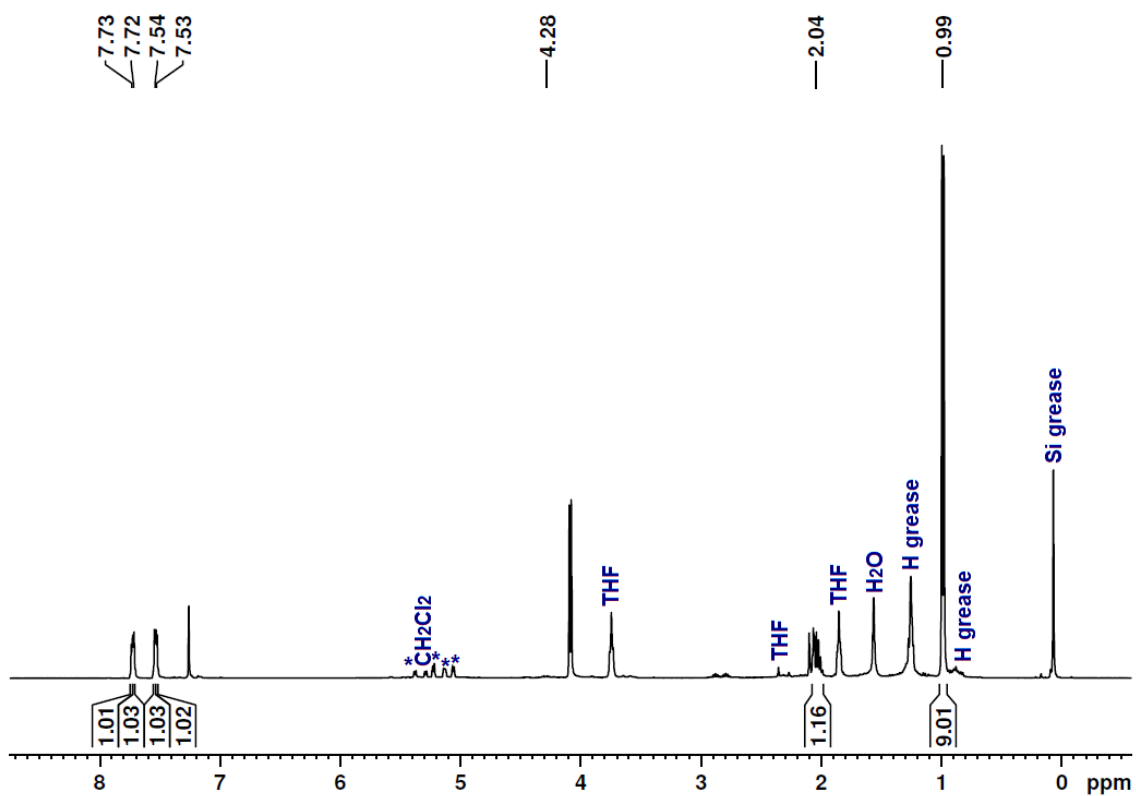


Fig. S6. ^1H NMR spectrum of **3** in CDCl_3 . (* = Inseparable impurity)

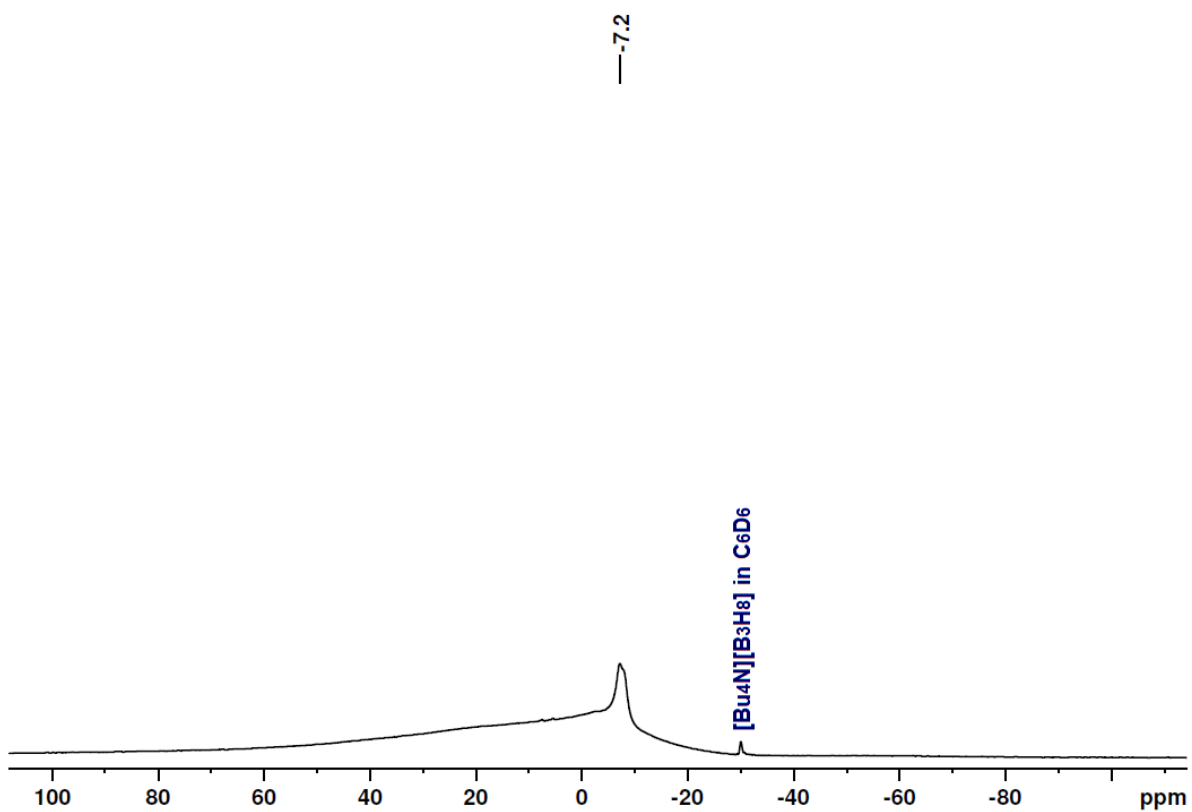


Fig. S7. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 .

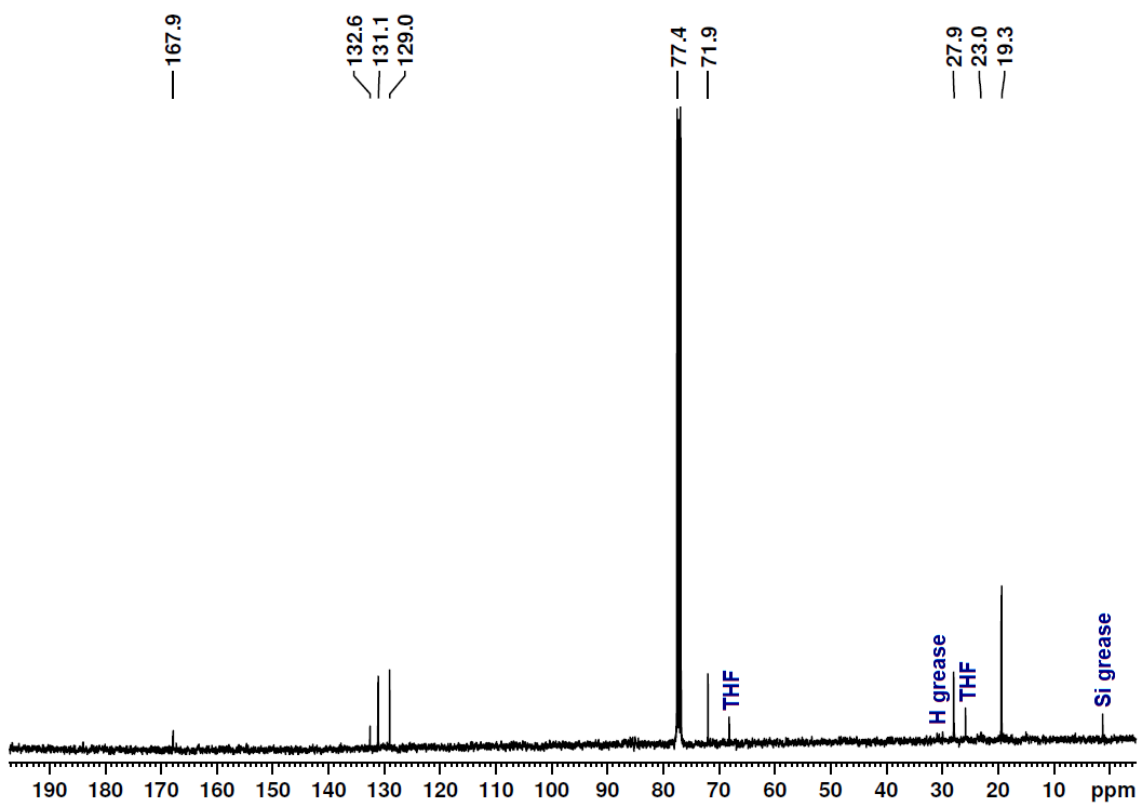


Fig. S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 .

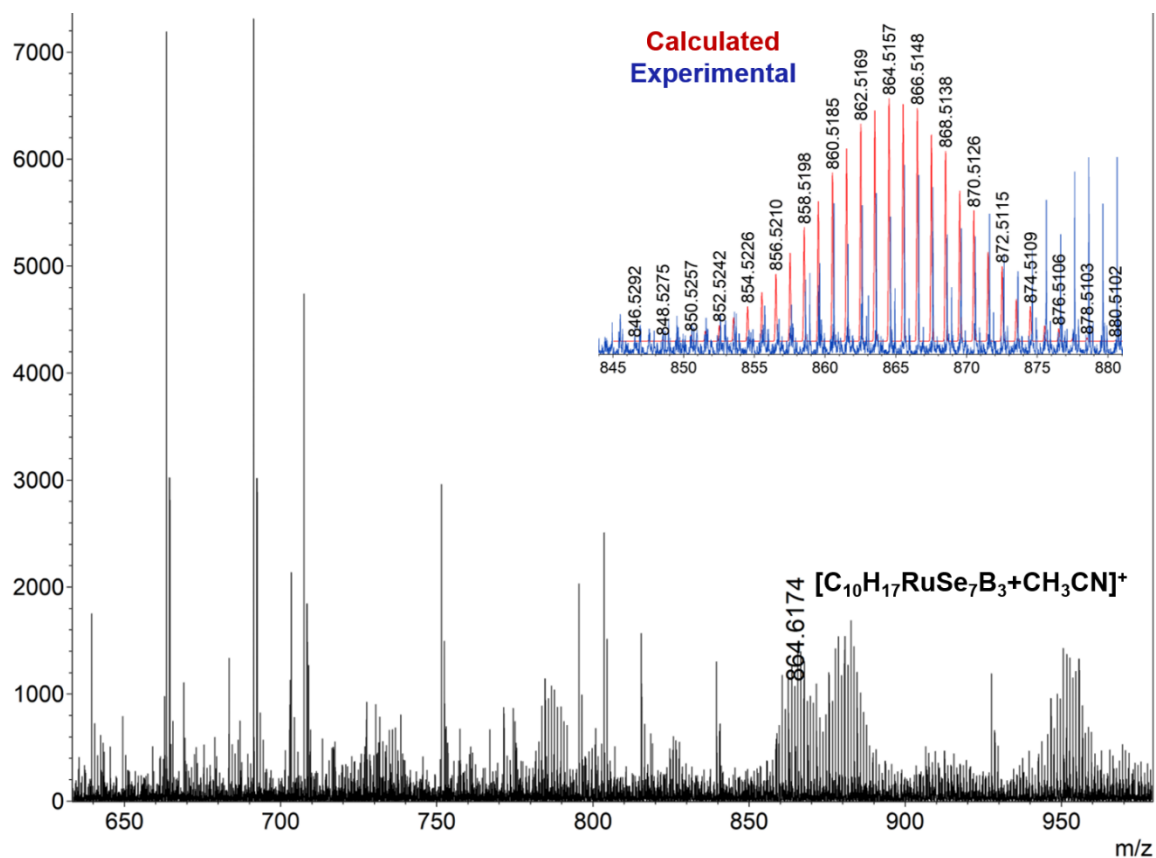


Fig. S9. ESI-MS spectrum of **3** in CH₂Cl₂-MeOH mixture.

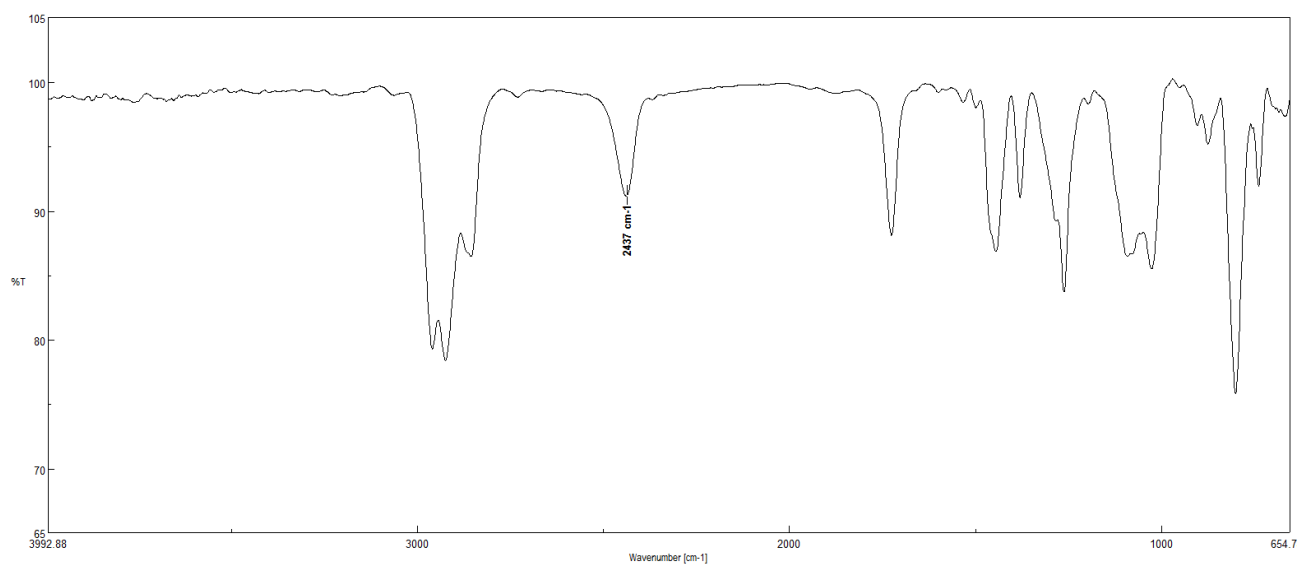


Fig. S10. IR spectrum of **3** in CH₂Cl₂.

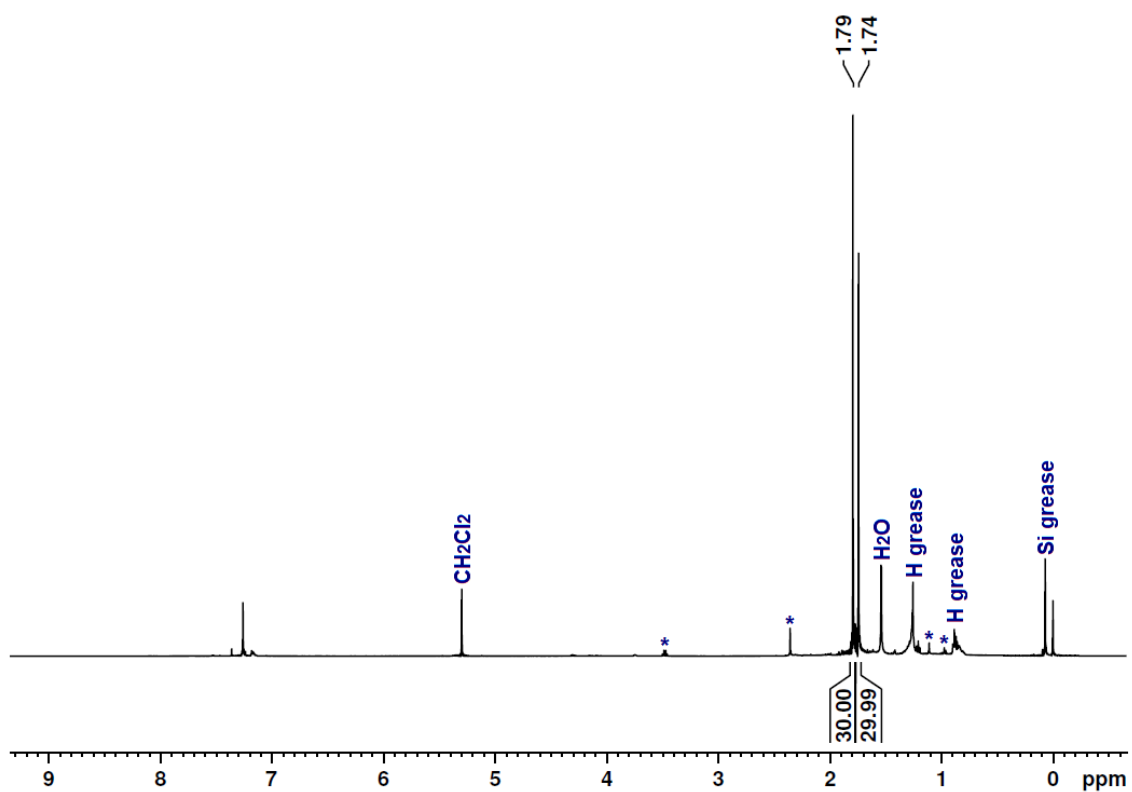


Fig. S11. Combined ^1H NMR spectrum of **4** and **5** in CDCl_3 . (* = Inseparable impurity)

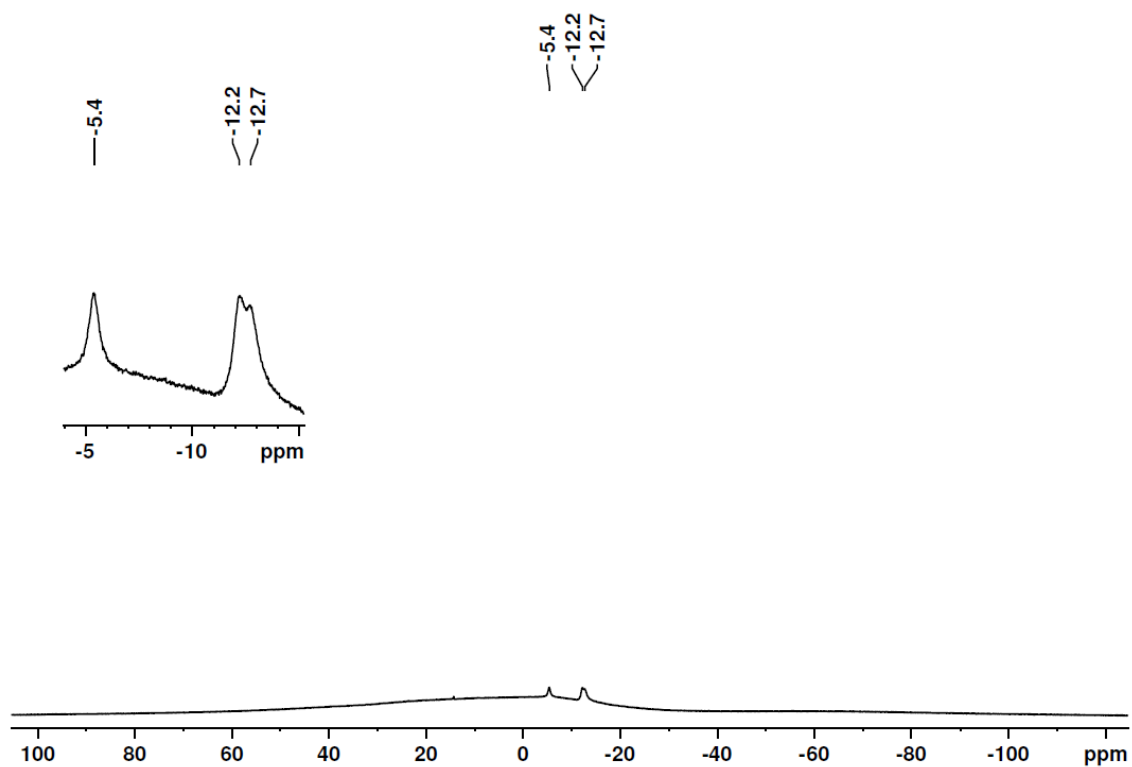


Fig. S12. Combined $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4** and **5** in CDCl_3 .

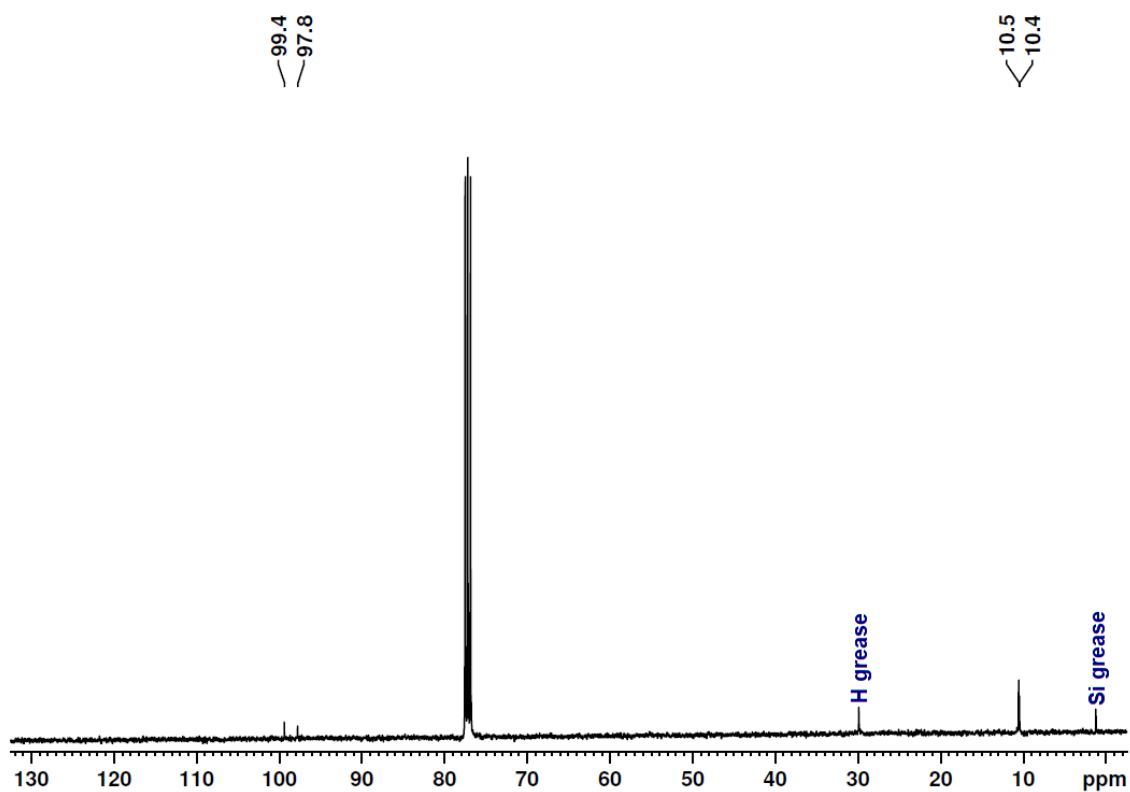


Fig. S13. Combined $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** and **5** in CDCl_3 .

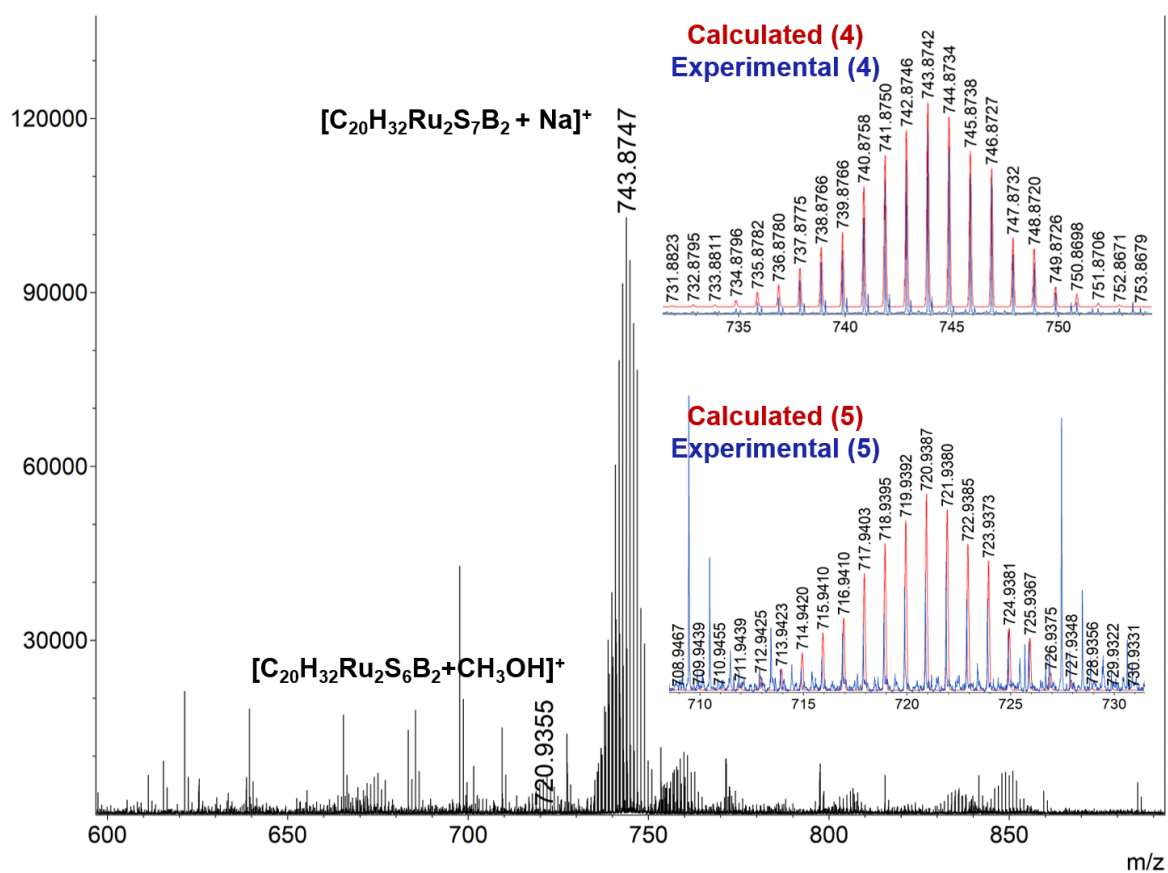


Fig. S14. Combined ESI-MS spectrum of **4** and **5** in CH_2Cl_2 -MeOH mixture.

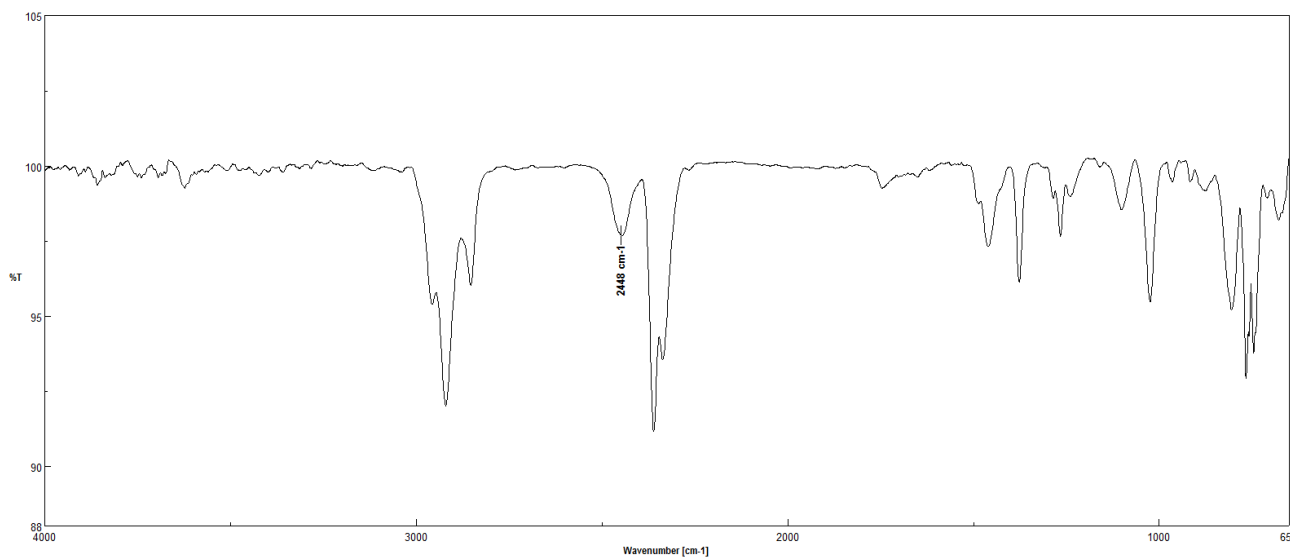


Fig. S15. Combined IR spectrum of **4** and **5** in CH₂Cl₂.

II Computational Details

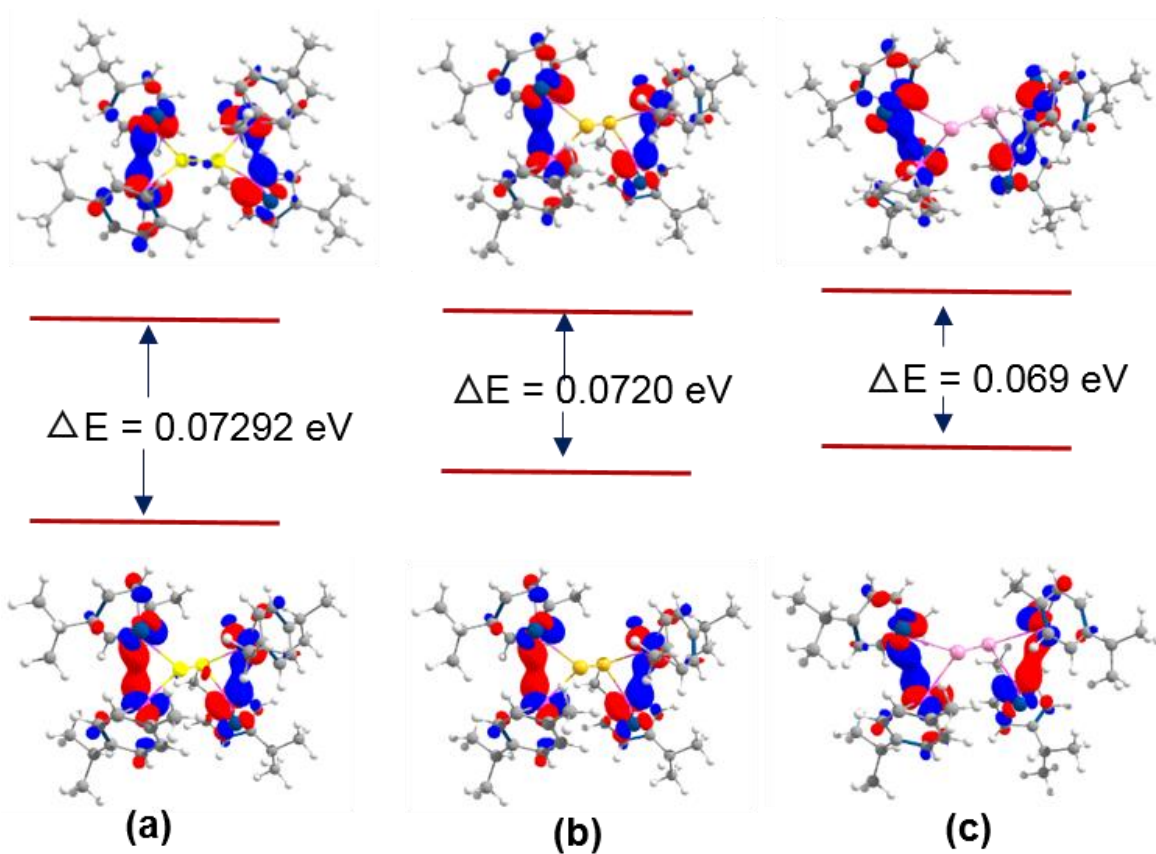


Fig. S16. HOMO-LUMO gap of (a) **1**, (b) **2** and (c) **2'**.

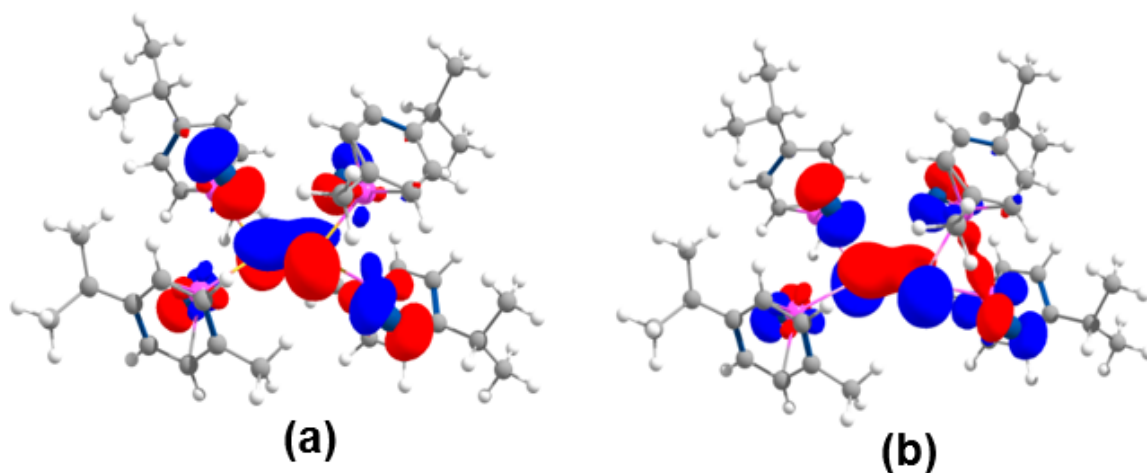


Fig. S17. (a) and (b) HOMO-13 involving E–E bonding interaction in **2** and **2'**, respectively.

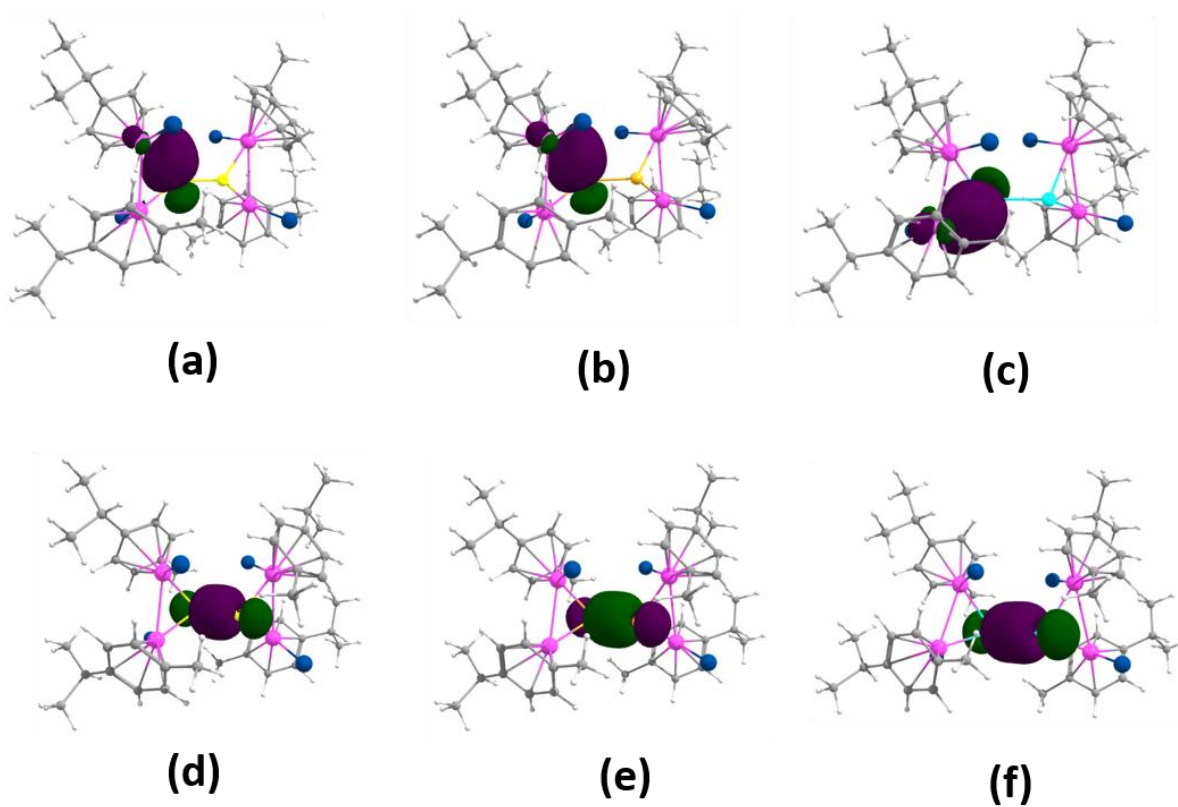


Fig. S18. Selected natural bonding orbitals of **1** (a,d), **2** (b,e) and **2'** (c,f).

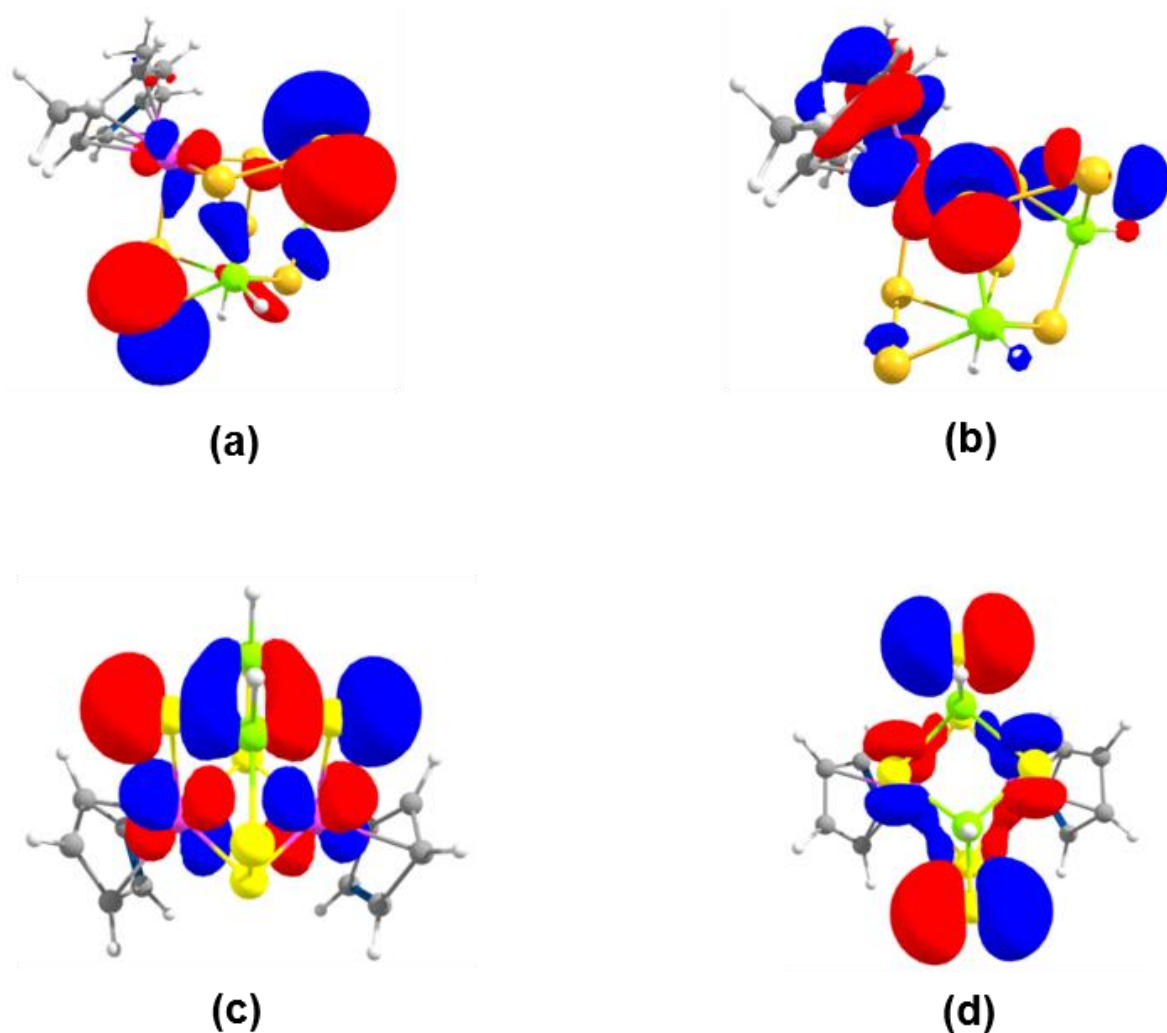


Fig. S19. Selected molecular orbitals of **3**, **4'** and **5'** (a) HOMO of **3**; (b) LUMO of **3**; (c) HOMO of **5'** and (d) HOMO-1 of **5'**.

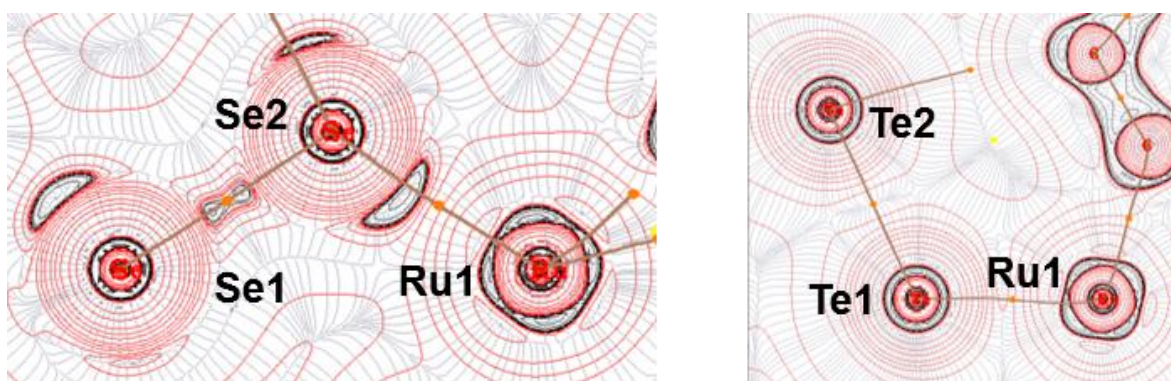


Fig. S20. Contour diagram of the Laplacian of the electron density, $\nabla^2\rho(r)$, of **2** (left) and **2'** (right) in the Ru1–Se1–Se2 and Ru1–Te1–Te2 planes respectively generated by the Multiwfn program at the B3LYP/SDD level of theory. The dashed black lines show areas of charge depletion [$-\nabla^2\rho(r) < 0$], and the solid red lines indicate areas of charge concentration [$-\nabla^2\rho(r) > 0$]. The solid brown lines indicate bond paths. The orange dots indicate BCPs.

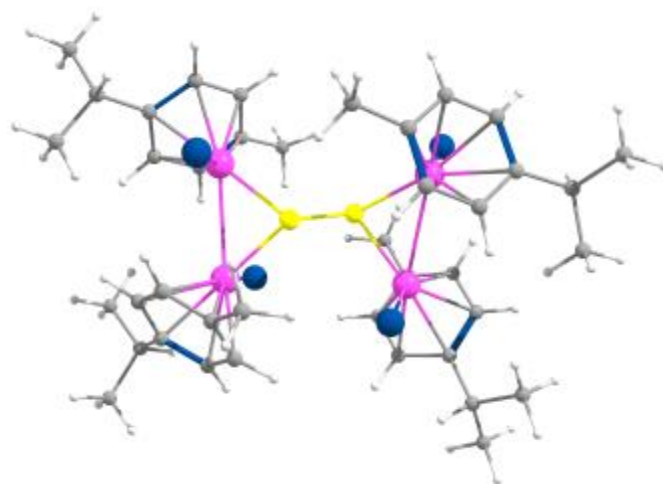


Fig. S21. Optimized geometry of **1**

Total energy = -4575.1613490 a.u.

Cartesian coordinates for the calculated structure **1** (in Å)

Ru	2.229551000	1.428569000	0.469554000	C	5.447205000	3.210463000	-1.232769000
Cl	1.595689000	2.014595000	-1.800281000	H	6.302775000	2.938787000	-0.601702000
C	2.244585000	1.754688000	2.696955000	H	5.833228000	3.823766000	-2.054301000
C	1.653835000	2.884804000	2.043990000	H	5.022268000	2.298493000	-1.663729000
H	0.631866000	3.163148000	2.279816000	Ru	2.752075000	-1.401765000	-0.134824000
C	2.369628000	3.586739000	1.042624000	Cl	3.063965000	-2.065954000	2.193693000
H	1.873001000	4.386715000	0.501941000	C	2.465312000	-1.744647000	-2.372800000
C	3.686147000	3.197050000	0.634056000	C	3.498662000	-0.799687000	-2.151149000
C	4.246916000	2.051110000	1.250330000	H	3.407523000	0.187544000	-2.588456000
H	5.210643000	1.674279000	0.928307000	C	4.620973000	-1.105815000	-1.318110000
C	3.534632000	1.340692000	2.267553000	H	5.368555000	-0.340895000	-1.147275000
H	3.955656000	0.430800000	2.679443000	C	4.747648000	-2.375237000	-0.698228000
C	1.502460000	1.015401000	3.778313000	C	3.676299000	-3.304594000	-0.876063000
H	1.823307000	-0.028406000	3.825563000	H	3.689255000	-4.232218000	-0.312136000
H	0.424189000	1.045920000	3.596651000	C	2.547498000	-2.992941000	-1.674737000
H	1.702842000	1.487030000	4.750200000	H	1.730056000	-3.702907000	-1.756512000
C	4.385178000	3.997281000	-0.453673000	C	1.343255000	-1.461866000	-3.334140000
H	3.605231000	4.287229000	-1.169505000	H	0.425743000	-1.988019000	-3.059503000
C	4.985180000	5.284186000	0.151461000	H	1.642141000	-1.796373000	-4.337885000
H	4.224904000	5.879151000	0.669792000	H	1.127666000	-0.392374000	-3.374203000
H	5.423478000	5.907796000	-0.636322000	C	5.928803000	-2.770417000	0.174227000
H	5.775562000	5.046572000	0.874200000	H	5.514482000	-3.350547000	1.008228000

C	6.692359000	-1.585686000	0.780093000	H	-6.470993000	2.754552000	0.938187000
H	7.198211000	-0.986596000	0.012290000	H	-5.920844000	3.631681000	2.366774000
H	7.465097000	-1.955839000	1.462633000	H	-5.147299000	2.097972000	1.936119000
H	6.020443000	-0.938035000	1.351514000	Ru	-2.480501000	1.198709000	-0.454800000
C	6.877825000	-3.686472000	-0.627731000	Cl	-1.986350000	1.478421000	1.888007000
H	6.354294000	-4.563804000	-1.023782000	C	-1.720675000	-3.180005000	1.489539000
H	7.694507000	-4.040639000	0.011796000	C	-2.280798000	-2.001739000	2.068026000
H	7.320543000	-3.148598000	-1.475223000	H	-1.654727000	-1.331830000	2.645326000
Ru	-2.570371000	-1.859234000	-0.130504000	C	-3.626366000	-1.627699000	1.797397000
Cl	-3.055106000	-2.231147000	-2.471186000	H	-3.984073000	-0.690554000	2.204381000
C	-2.658613000	1.643982000	-2.667993000	C	-4.482397000	-2.446871000	0.991380000
C	-3.910615000	1.210793000	-2.153400000	C	-3.898666000	-3.593380000	0.390881000
H	-4.375259000	0.326871000	-2.577009000	H	-4.472804000	-4.156932000	-0.337654000
C	-4.550904000	1.899368000	-1.072540000	C	-2.549529000	-3.960179000	0.629013000
H	-5.507603000	1.538202000	-0.715998000	H	-2.125630000	-4.811196000	0.105493000
C	-3.929687000	3.003997000	-0.442687000	C	-0.318176000	-3.625208000	1.798203000
C	-2.624692000	3.374131000	-0.897115000	H	-0.345371000	-4.331120000	2.640257000
H	-2.074985000	4.137030000	-0.354604000	H	0.334465000	-2.796349000	2.074003000
C	-1.998750000	2.713154000	-1.984995000	H	0.132338000	-4.143351000	0.946034000
H	-0.983318000	2.976582000	-2.261704000	C	-5.960839000	-2.167827000	0.753392000
C	-2.015989000	0.985019000	-3.858340000	H	-6.130635000	-2.257592000	-0.328326000
H	-2.286200000	-0.071861000	-3.916821000	C	-6.412850000	-0.772537000	1.195413000
H	-0.927083000	1.068882000	-3.804939000	H	-6.369689000	-0.661916000	2.285925000
H	-2.352113000	1.485940000	-4.776708000	H	-7.451032000	-0.601111000	0.890117000
C	-4.550082000	3.790055000	0.701617000	H	-5.790158000	0.007625000	0.752089000
H	-3.724797000	4.050543000	1.376708000	C	-6.811815000	-3.249795000	1.454317000
C	-5.151725000	5.101361000	0.151364000	H	-6.664705000	-3.217585000	2.540785000
H	-4.408436000	5.688363000	-0.399710000	H	-6.555809000	-4.257098000	1.109355000
H	-5.530029000	5.719817000	0.973408000	H	-7.876370000	-3.084263000	1.252069000
H	-5.987382000	4.894505000	-0.528496000	S	0.783627000	-0.395109000	0.631684000
C	-5.582591000	3.014012000	1.527401000	S	-0.851835000	-0.426061000	-0.834312000

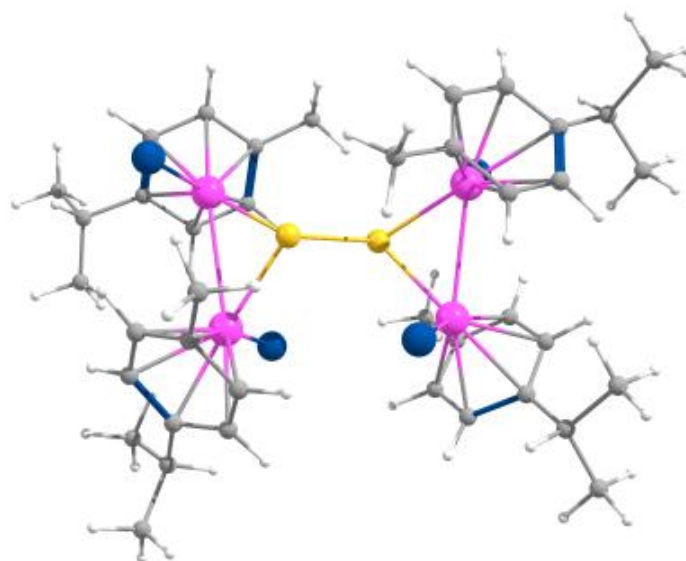


Fig. S22. Optimized geometry of **2**

Total energy = -8576.6744564 a.u.

Cartesian coordinates for the calculated structure **2** (in Å)

Ru	2.302647000	1.430223000	0.518357000	C	5.458277000	3.325043000	-1.184161000
Cl	1.599742000	2.032457000	-1.727946000	H	6.326916000	3.056887000	-0.569638000
C	2.337881000	1.707256000	2.750007000	H	5.821162000	3.966371000	-1.994763000
C	1.713412000	2.837434000	2.129600000	H	5.048158000	2.414642000	-1.632352000
H	0.689556000	3.090837000	2.384768000	Ru	2.960471000	-1.400569000	-0.171304000
C	2.400193000	3.574897000	1.132501000	Cl	3.247931000	-2.143266000	2.136840000
H	1.878838000	4.375130000	0.615987000	C	2.717816000	-1.640913000	-2.419410000
C	3.721820000	3.226987000	0.702996000	C	3.704330000	-0.661529000	-2.137192000
C	4.315738000	2.080374000	1.286607000	H	3.569969000	0.341142000	-2.526000000
H	5.283933000	1.732929000	0.945720000	C	4.832925000	-0.958904000	-1.309280000
C	3.630756000	1.329591000	2.294011000	H	5.544095000	-0.171085000	-1.092329000
H	4.075834000	0.419126000	2.679289000	C	5.006261000	-2.248408000	-0.745475000
C	1.631384000	0.930976000	3.830171000	C	3.980957000	-3.216681000	-0.984255000
H	1.961643000	-0.111302000	3.841119000	H	4.028439000	-4.168886000	-0.464866000
H	0.547722000	0.956740000	3.681778000	C	2.851036000	-2.919422000	-1.786902000
H	1.854812000	1.376375000	4.809290000	H	2.070994000	-3.663288000	-1.917392000
C	4.388403000	4.068449000	-0.373934000	C	1.595422000	-1.358871000	-3.380872000
H	3.592684000	4.356228000	-1.073279000	H	0.712310000	-1.964173000	-3.162070000
C	4.965874000	5.355018000	0.253388000	H	1.928644000	-1.599119000	-4.400504000
H	4.198586000	5.919424000	0.795018000	H	1.310705000	-0.305004000	-3.347771000
H	5.379179000	6.007089000	-0.524830000	C	6.189050000	-2.630726000	0.130430000
H	5.770845000	5.119484000	0.960528000	H	5.786859000	-3.268801000	0.927357000

C	6.883893000	-1.442341000	0.807559000	H	-6.357243000	3.090035000	1.074997000
H	7.377123000	-0.785418000	0.079861000	H	-5.656645000	3.934337000	2.456689000
H	7.658630000	-1.808130000	1.490167000	H	-5.025389000	2.344417000	1.997166000
H	6.170162000	-0.853803000	1.392036000	Ru	-2.573721000	1.241741000	-0.520982000
C	7.194868000	-3.462320000	-0.693761000	Cl	-1.978337000	1.469728000	1.800584000
H	6.720720000	-4.342990000	-1.141271000	C	-1.902215000	-3.273584000	1.418138000
H	8.015680000	-3.808480000	-0.055119000	C	-2.324894000	-2.062596000	2.045227000
H	7.626854000	-2.864392000	-1.505817000	H	-1.603021000	-1.438047000	2.558344000
Ru	-2.809074000	-1.908960000	-0.116773000	C	-3.659478000	-1.594248000	1.895789000
Cl	-3.520726000	-2.217345000	-2.402779000	H	-3.908850000	-0.630440000	2.321169000
C	-2.860747000	1.651155000	-2.728536000	C	-4.643592000	-2.351114000	1.178664000
C	-4.102920000	1.313756000	-2.124238000	C	-4.203389000	-3.539513000	0.539719000
H	-4.649948000	0.453454000	-2.495316000	H	-4.881883000	-4.062064000	-0.127374000
C	-4.626192000	2.065591000	-1.023160000	C	-2.863010000	-3.994394000	0.645149000
H	-5.578663000	1.774564000	-0.597236000	H	-2.549304000	-4.869303000	0.084677000
C	-3.892354000	3.136593000	-0.457854000	C	-0.506716000	-3.812437000	1.585078000
C	-2.594561000	3.404171000	-0.997652000	H	-0.489064000	-4.506753000	2.436531000
H	-1.959142000	4.136622000	-0.509688000	H	0.222463000	-3.024123000	1.779718000
C	-2.086104000	2.681669000	-2.110130000	H	-0.187968000	-4.366392000	0.696493000
H	-1.073654000	2.871624000	-2.451631000	C	-6.110851000	-1.959832000	1.071956000
C	-2.350094000	0.925913000	-3.944893000	H	-6.398078000	-2.097702000	0.020611000
H	-2.684905000	-0.114423000	-3.952987000	C	-6.400519000	-0.506008000	1.459205000
H	-1.257046000	0.943743000	-3.980714000	H	-6.243085000	-0.334701000	2.531093000
H	-2.727207000	1.422401000	-4.849453000	H	-7.445751000	-0.261672000	1.239479000
C	-4.384147000	3.978888000	0.708485000	H	-5.759879000	0.186843000	0.908279000
H	-3.502876000	4.186129000	1.329127000	C	-6.965604000	-2.923752000	1.923951000
C	-4.922890000	5.324054000	0.175393000	H	-6.704074000	-2.841266000	2.985969000
H	-4.174092000	5.850578000	-0.426966000	H	-6.824236000	-3.967067000	1.622132000
H	-5.206604000	5.976504000	1.009160000	H	-8.029565000	-2.682194000	1.817899000
H	-5.810307000	5.170567000	-0.450862000	Se	-0.966650000	-0.537497000	-1.007679000
C	-5.417346000	3.287111000	1.605631000	Se	0.838365000	-0.515477000	0.679651000

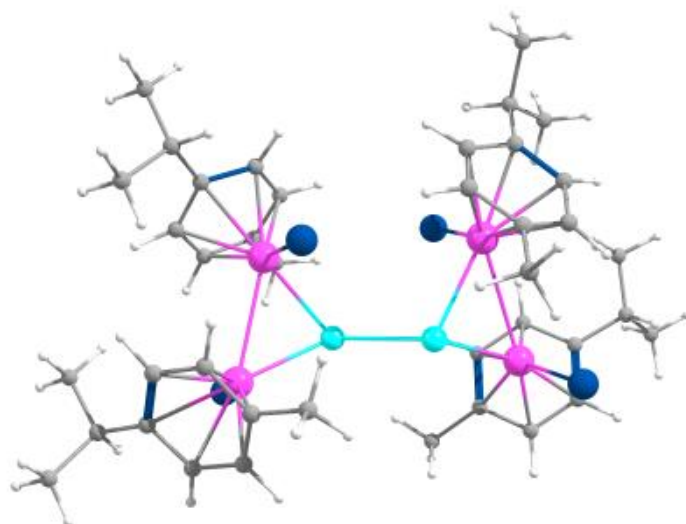


Fig. S23. Optimized geometry of **2'**

Total energy = -3795.51779016 a.u.

Cartesian coordinates for the calculated structure **2'** (in Å)

Ru	-3.400314000	-1.417239000	0.178090000	H	-5.478936000	4.272045000	2.116573000
Cl	-1.574614000	1.849251000	1.637045000	H	-4.925921000	2.637199000	1.720006000
C	-2.577814000	1.617749000	-2.812573000	Ru	-2.415974000	1.343597000	-0.580185000
C	-1.789122000	2.668205000	-2.241761000	Cl	-3.819962000	-2.120457000	-2.118781000
H	-0.762938000	2.807941000	-2.565861000	C	-3.145923000	-1.658722000	2.414227000
C	-2.319808000	3.480087000	-1.207097000	C	-3.998009000	-0.557968000	2.139792000
H	-1.679840000	4.220110000	-0.736286000	H	-3.720776000	0.422295000	2.509457000
C	-3.641463000	3.283360000	-0.690412000	C	-5.173900000	-0.709886000	1.339188000
C	-4.396655000	2.207644000	-1.220321000	H	-5.776880000	0.164039000	1.125806000
H	-5.372785000	1.971732000	-0.813558000	C	-5.529095000	-1.969685000	0.792851000
C	-3.866782000	1.381851000	-2.261437000	C	-4.641237000	-3.067022000	1.028564000
H	-4.434823000	0.526189000	-2.608818000	H	-4.826648000	-4.009906000	0.523259000
C	-2.053436000	0.784785000	-3.953230000	C	-3.466914000	-2.916511000	1.807036000
H	-2.470099000	-0.225834000	-3.925931000	H	-2.792060000	-3.757909000	1.930705000
H	-0.961958000	0.716376000	-3.922040000	C	-1.964511000	-1.516747000	3.335065000
H	-2.337450000	1.249737000	-4.907320000	H	-1.180365000	-2.241522000	3.099205000
C	-4.138272000	4.198526000	0.417431000	H	-2.286726000	-1.694354000	4.370781000
H	-3.275261000	4.385948000	1.069537000	H	-1.538664000	-0.512704000	3.272701000
C	-4.587997000	5.547016000	-0.184182000	C	-6.770391000	-2.199529000	-0.054868000
H	-3.789152000	6.013651000	-0.771311000	H	-6.473162000	-2.891088000	-0.853331000
H	-4.873694000	6.243873000	0.612348000	C	-7.319836000	-0.935966000	-0.729327000
H	-5.454403000	5.412943000	-0.843604000	H	-7.704124000	-0.213635000	0.002092000
C	-5.244412000	3.592048000	1.290312000	H	-8.152894000	-1.202530000	-1.388846000
H	-6.172664000	3.434899000	0.726608000	H	-6.550726000	-0.450924000	-1.338114000

C	-7.857931000	-2.886411000	0.798531000	H	4.744512000	2.774298000	-2.053913000
H	-7.492988000	-3.817957000	1.245336000	Ru	2.641435000	1.272700000	0.597645000
H	-8.730462000	-3.127461000	0.180443000	Cl	1.903080000	1.410299000	-1.681012000
H	-8.190664000	-2.230917000	1.612929000	C	2.561710000	-3.292339000	-1.477014000
Ru	3.336511000	-1.864988000	0.058140000	C	2.767207000	-2.016296000	-2.082005000
Cl	4.215686000	-2.078708000	2.288569000	H	1.937146000	-1.492210000	-2.542037000
C	3.069811000	1.680270000	2.787431000	C	4.023851000	-1.357925000	-1.977418000
C	4.284768000	1.541836000	2.061216000	H	4.102952000	-0.353725000	-2.374265000
H	4.985713000	0.767846000	2.355867000	C	5.146668000	-1.980291000	-1.339868000
C	4.588757000	2.385527000	0.945508000	C	4.921081000	-3.239440000	-0.723429000
H	5.530729000	2.250245000	0.428695000	H	5.704722000	-3.675466000	-0.111393000
C	3.653123000	3.341055000	0.478756000	C	3.658144000	-3.886376000	-0.778544000
C	2.382654000	3.397210000	1.135385000	H	3.506863000	-4.814344000	-0.236227000
H	1.600628000	4.030751000	0.729205000	C	1.251083000	-4.026247000	-1.586692000
C	2.095545000	2.588736000	2.269128000	H	1.302769000	-4.738573000	-2.421577000
H	1.103445000	2.626542000	2.707137000	H	0.417965000	-3.346132000	-1.776885000
C	2.804607000	0.879667000	4.034981000	H	1.036574000	-4.592640000	-0.675028000
H	3.278644000	-0.103819000	3.981463000	C	6.542718000	-1.375293000	-1.290327000
H	1.731560000	0.741566000	4.196991000	H	6.901679000	-1.493444000	-0.258800000
H	3.210762000	1.415727000	4.903733000	C	6.591373000	0.114801000	-1.644542000
C	3.904753000	4.263656000	-0.703154000	H	6.354067000	0.286278000	-2.701612000
H	2.960074000	4.311136000	-1.260219000	H	7.598556000	0.508183000	-1.467762000
C	4.229268000	5.681849000	-0.186135000	H	5.884540000	0.690011000	-1.041412000
H	3.441278000	6.063746000	0.472593000	C	7.487500000	-2.177663000	-2.211952000
H	4.334365000	6.377229000	-1.026838000	H	7.163254000	-2.108842000	-3.257535000
H	5.170418000	5.688135000	0.377283000	H	7.519163000	-3.237651000	-1.937979000
C	4.982610000	3.772928000	-1.677178000	H	8.507427000	-1.781225000	-2.147314000
H	5.976656000	3.751533000	-1.213052000	Te	-1.006763000	-0.859977000	-0.801209000
H	5.040635000	4.453175000	-2.534104000	Te	1.163560000	-0.825737000	1.183695000

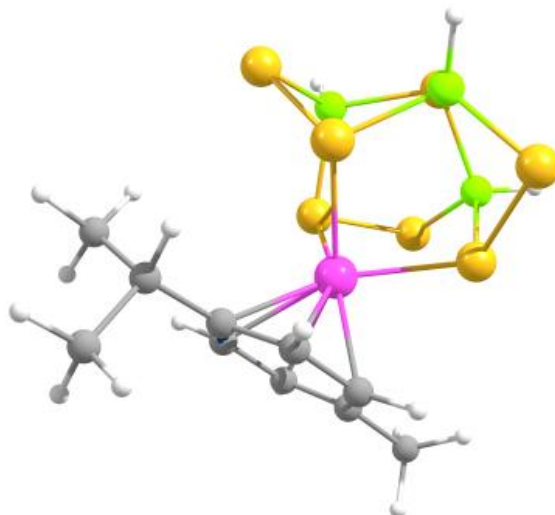


Fig. S24. Optimized geometry of **3**

Total energy = -17353.6201976 a.u.

Cartesian coordinates for the calculated structure **3** (in Å)

Ru	-1.013948000	-0.720297000	-0.003838000	H	-1.901634000	-5.000847000	-0.179635000
Se	1.133076000	-1.630673000	0.924045000	H	-0.658455000	-4.276682000	-1.220990000
Se	1.616150000	-0.316414000	2.865011000	C	-4.128630000	0.929171000	0.265034000
Se	2.640313000	1.252905000	0.026599000	H	-3.679066000	1.477886000	1.103583000
Se	-0.163621000	3.049617000	-0.624722000	C	-4.130258000	1.857559000	-0.956547000
Se	0.220838000	0.094370000	-2.038882000	H	-4.661618000	2.782894000	-0.710853000
Se	2.170904000	-1.288079000	-2.184415000	H	-3.114196000	2.126527000	-1.262725000
Se	-0.547806000	1.469646000	1.136814000	H	-4.649521000	1.404652000	-1.810247000
C	-2.971199000	-0.879045000	-1.172936000	C	-5.568718000	0.545641000	0.672143000
H	-3.220181000	-0.338162000	-2.078348000	H	-5.587554000	-0.077430000	1.573272000
C	-3.308903000	-0.339430000	0.086706000	H	-6.153556000	1.449289000	0.874996000
C	-2.864385000	-1.060780000	1.250846000	H	-6.068314000	-0.007451000	-0.132256000
H	-3.043650000	-0.640607000	2.235861000	B	2.654152000	-0.821083000	-0.271083000
C	-2.173446000	-2.284203000	1.139118000	B	1.456406000	1.372465000	1.754519000
H	-1.827172000	-2.785347000	2.038075000	B	1.239565000	1.823783000	-1.423986000
C	-1.873625000	-2.856373000	-0.145600000	H	3.693817000	-1.304184000	0.063712000
C	-2.257615000	-2.117117000	-1.285586000	H	1.703413000	2.356742000	2.383872000
H	-1.984283000	-2.480131000	-2.271763000	H	1.771368000	2.306104000	-2.378315000
C	-1.172897000	-4.183986000	-0.260404000				
H	-0.433256000	-4.311286000	0.535479000				

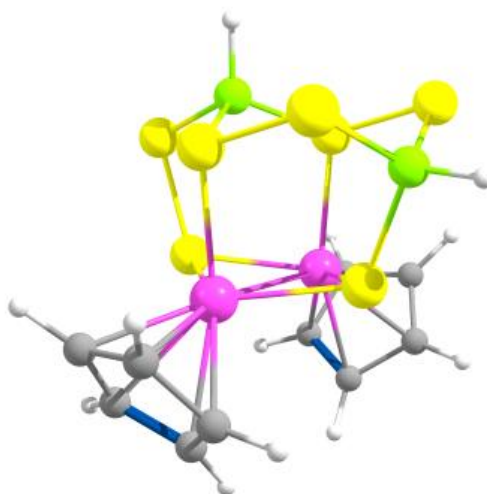


Fig. S25. Optimized geometry of **4'**

Total energy = - 3415.45344849 a.u.

Cartesian coordinates for the calculated structure **4'** (in Å)

C	-2.134617000	-2.577779000	-0.989437000	B	-0.000052000	2.309696000	-1.756217000
C	-2.742852000	-1.483954000	-1.682742000	S	-1.651334000	1.642757000	0.744901000
C	-3.520476000	-0.730312000	-0.755212000	S	-1.624796000	2.911382000	-0.956151000
C	-3.395420000	-1.355657000	0.532766000	S	1.651075000	1.642795000	0.744979000
C	-2.542121000	-2.496152000	0.374205000	S	1.624624000	2.911446000	-0.956068000
C	2.135101000	-2.577429000	-0.989797000	H	-0.000048000	2.669482000	-2.903446000
C	2.542254000	-2.496175000	0.373936000	H	4.092960000	0.160030000	-0.980742000
C	3.395383000	-1.355638000	0.533046000	H	3.879931000	-1.038063000	1.446505000
C	3.520706000	-0.729912000	-0.754708000	H	2.242266000	-3.171555000	1.164917000
C	2.743367000	-1.483316000	-1.682634000	H	1.496204000	-3.333041000	-1.425644000
B	-0.000156000	1.986466000	1.744026000	H	2.610444000	-1.245709000	-2.729723000
H	-0.000149000	3.099368000	2.178813000	H	-2.242198000	-3.171243000	1.165456000
S	-0.000008000	0.299272000	-1.738958000	H	-1.495528000	-3.333462000	-1.424882000
S	-0.000003000	-0.986249000	1.735619000	H	-2.609653000	-1.246611000	-2.729855000
S	-0.000096000	0.662463000	3.094314000	H	-4.092793000	0.159483000	-0.981663000
Ru	-1.395017000	-0.586594000	-0.075234000	H	-3.880266000	-1.037903000	1.446006000
Ru	1.395029000	-0.586485000	-0.075209000				



Fig. S26. Optimized geometry of **5'**

Total energy = -3017.25782663 a.u.

Cartesian coordinates for the calculated structure **5'** (in Å)

C	2.753145000	-1.827184000	1.137965000	Ru	-1.401455000	-0.387488000	-0.002408000
C	3.478278000	-0.655628000	0.752006000	B	-0.002279000	2.542843000	1.231435000
C	3.507592000	-0.619918000	-0.684902000	S	1.462811000	2.039829000	0.003174000
C	2.799246000	-1.766748000	-1.158774000	S	-1.462675000	2.039889000	-0.002755000
C	2.329620000	-2.516579000	-0.037259000	S	-0.005160000	1.553156000	2.822701000
C	-2.329753000	-2.516480000	0.038003000	H	-0.002670000	3.723172000	1.433100000
C	-2.752560000	-1.827792000	-1.137866000	H	1.770074000	-3.441237000	-0.072798000
C	-3.477864000	-0.655933000	-0.753017000	H	2.540559000	-2.125750000	2.156326000
C	-3.508040000	-0.619418000	0.683850000	H	3.934206000	0.065061000	1.417251000
C	-2.799995000	-1.765944000	1.158815000	H	3.985018000	0.135547000	-1.294159000
B	0.002406000	2.543105000	-1.230933000	H	2.625963000	-2.011068000	-2.198800000
H	0.002846000	3.723483000	-1.432306000	H	-2.539402000	-2.126989000	-2.155922000
S	-0.002026000	-0.324543000	1.853012000	H	-3.933506000	0.064317000	-1.418932000
S	0.002016000	-0.324153000	-1.853110000	H	-3.985679000	0.136495000	1.292383000
S	0.005224000	1.553787000	-2.822396000	H	-2.627281000	-2.009633000	2.199084000
Ru	1.401419000	-0.387506000	0.002291000	H	-1.770219000	-3.441109000	0.074449000

Table S1. Selected geometrical parameters and Wiberg bond indices (WBI) of **1-5'**.

1				2			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Ru1-Ru2	2.939	2.940	0.413	Ru1-Ru2	-	2.986	0.399
Ru3-Ru4	2.939	3.076	0.347	Ru3-Ru4	-	3.185	0.311
Ru1-S1	2.320	2.332	0.791	Ru1-Se1	-	2.440	0.829
Ru1-Cl1	2.395	2.428	0.734	Ru1-Cl1	-	2.429	0.739
S1-S2	2.108	2.196	0.879	Se1-Se2	-	2.470	0.783
2'				3			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Ru1-Ru2	-	3.027	0.389	Ru1-Se1	2.473	2.509	0.820
Ru3-Ru4	-	3.248	0.293	Se1-B1	2.076	2.097	0.891
Ru1-Te1	-	2.645	0.849	Se3-B1	2.054	2.095	0.915
Ru1-Cl1	-	2.438	0.736	Se6-B1	2.020	2.087	1.053
Te1-Te2	-	2.941	0.747	Se1-Se2	2.362	2.393	0.916
4 and 4'				5 and 5'			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Ru1-Ru2	2.781	2.802	0.420	Ru1-Ru2	2.781	2.361	0.499
Ru1-S1'	2.383	2.428	0.752	Ru1-S1	2.382	2.507	0.627
Ru1-S3	2.298	2.323	0.805	Ru1-S3	2.298	2.154	0.718
B1-S1'	1.956	2.977	0.863	B1-S1'	1.918	2.355	0.769
B1-S7	1.867	2.873	1.045	B1-S7	1.867	2.790	0.879

Table S2. Calculated natural charges (q), natural valence population on E (p_E) and wiberg bond indices(WBI) of **1**, S_2 , S_2^{2-} , **2**, Se_2 , Se_2^{2-} , **2'**, Te_2 and Te_2^{2-} .

Compound	Natural charge on E(q_E)	Natural valence population on E(p_E)	WBI of E-E bond
1	0.290	5.720	0.879
S_2	0	5.955	2.038
S_2^{2-}	-1.000	6.977	1.021
2	0.394	5.575	0.783
Se_2	0	5.965	2.026
Se_2^{2-}	-1.000	6.988	1.012
2'	0.536	5.452	0.747
Te_2	0	5.968	2.031
Te_2^{2-}	-1.000	6.971	1.037

Table S3. Calculated natural charges (q) of **1**, **2** and **2'**.

Compound	q_{Ru1}	q_{Ru2}	q_{Ru3}	q_{Ru4}	q_{E1}	q_{E2}
1	-0.311	-0.314	-0.299	-0.295	0.290	0.289
2	-0.360	-0.365	-0.340	-0.335	0.386	0.403
2'	-0.429	-0.432	-0.401	-0.410	0.548	0.523