Supporting Information for

Self-assembly of a new class of rhenium(I)-based double stranded dinuclear monohelicates with their photophysical and electrochemical studies

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Contents

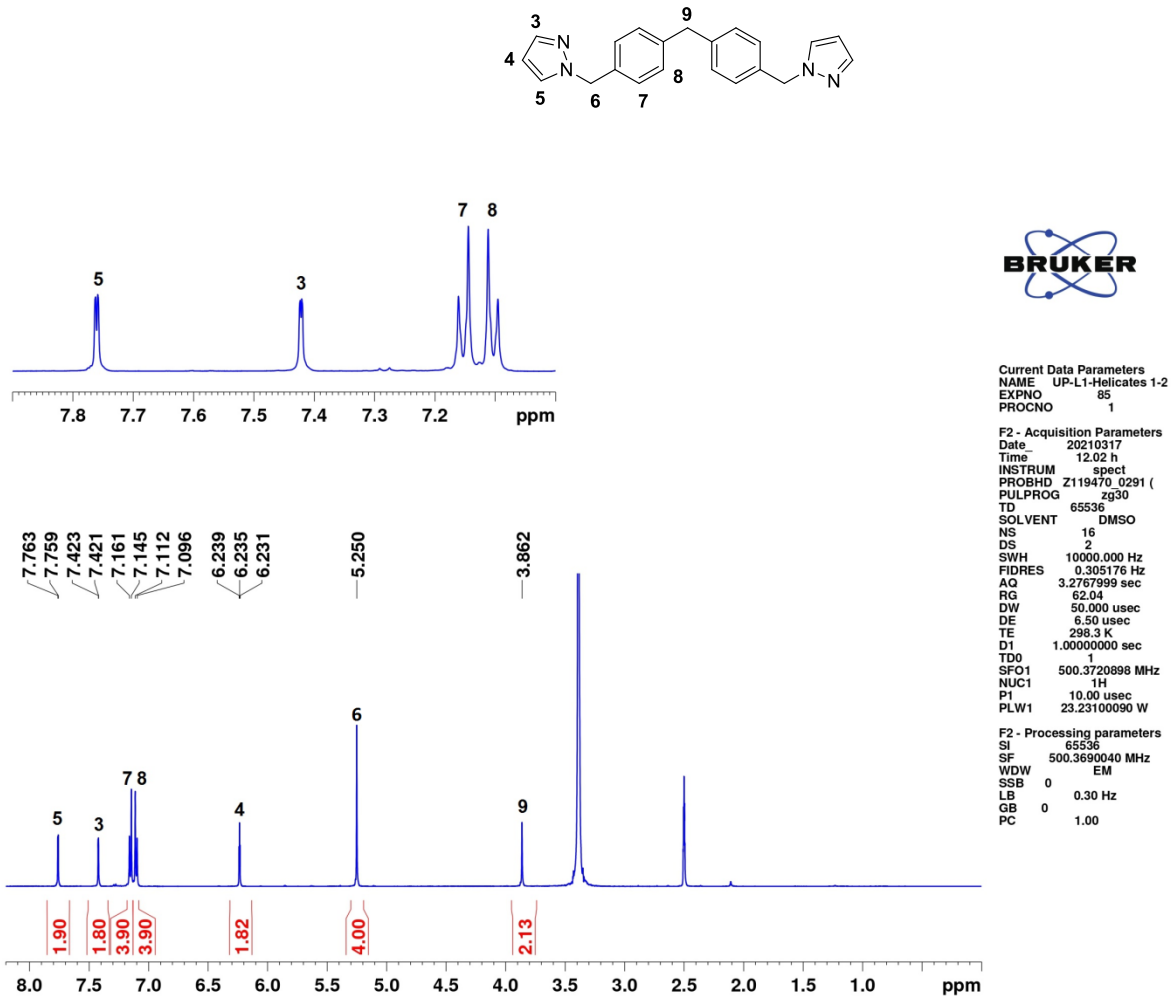

Figure S1. ^{1}H NMR spectrum of L^{1} in DMSO–d_6.

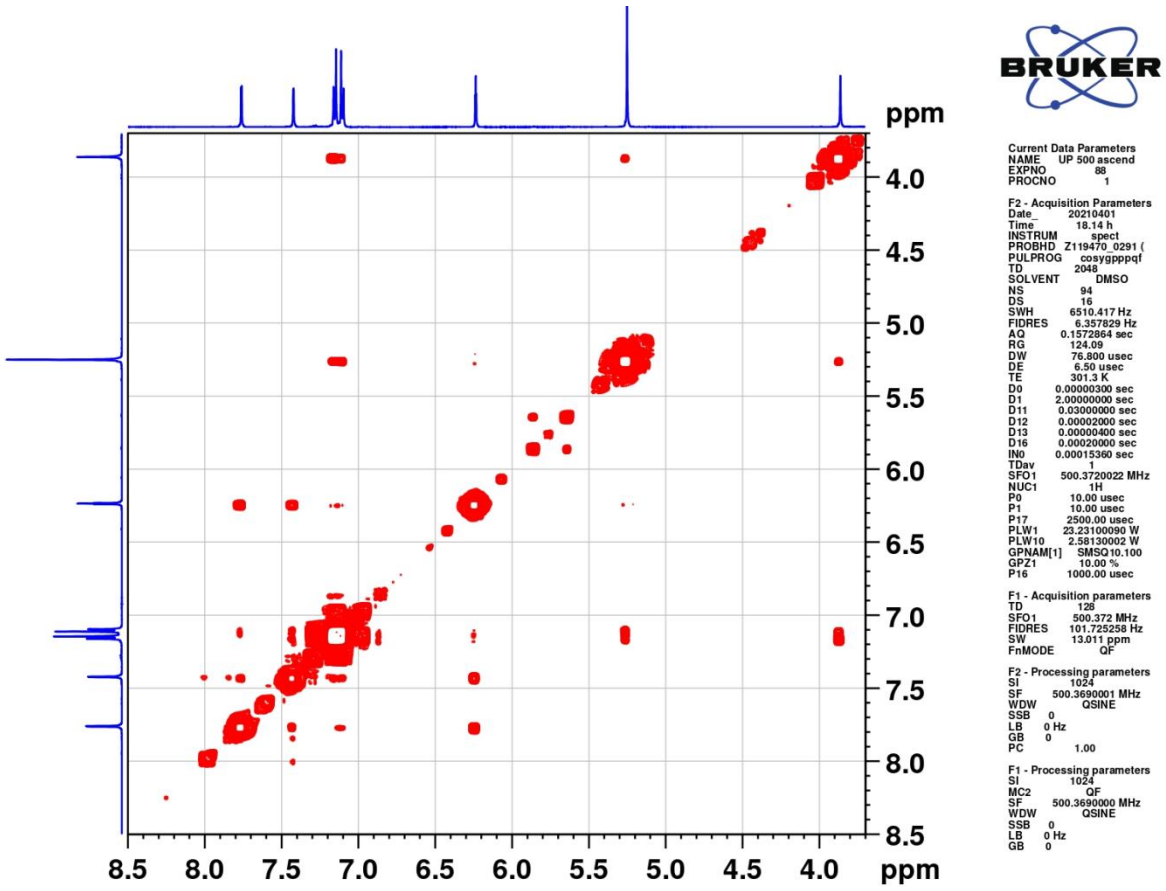

Figure S2. ^{1}H–^{1}H COSY NMR spectrum of L^{1} in DMSO–d_6.

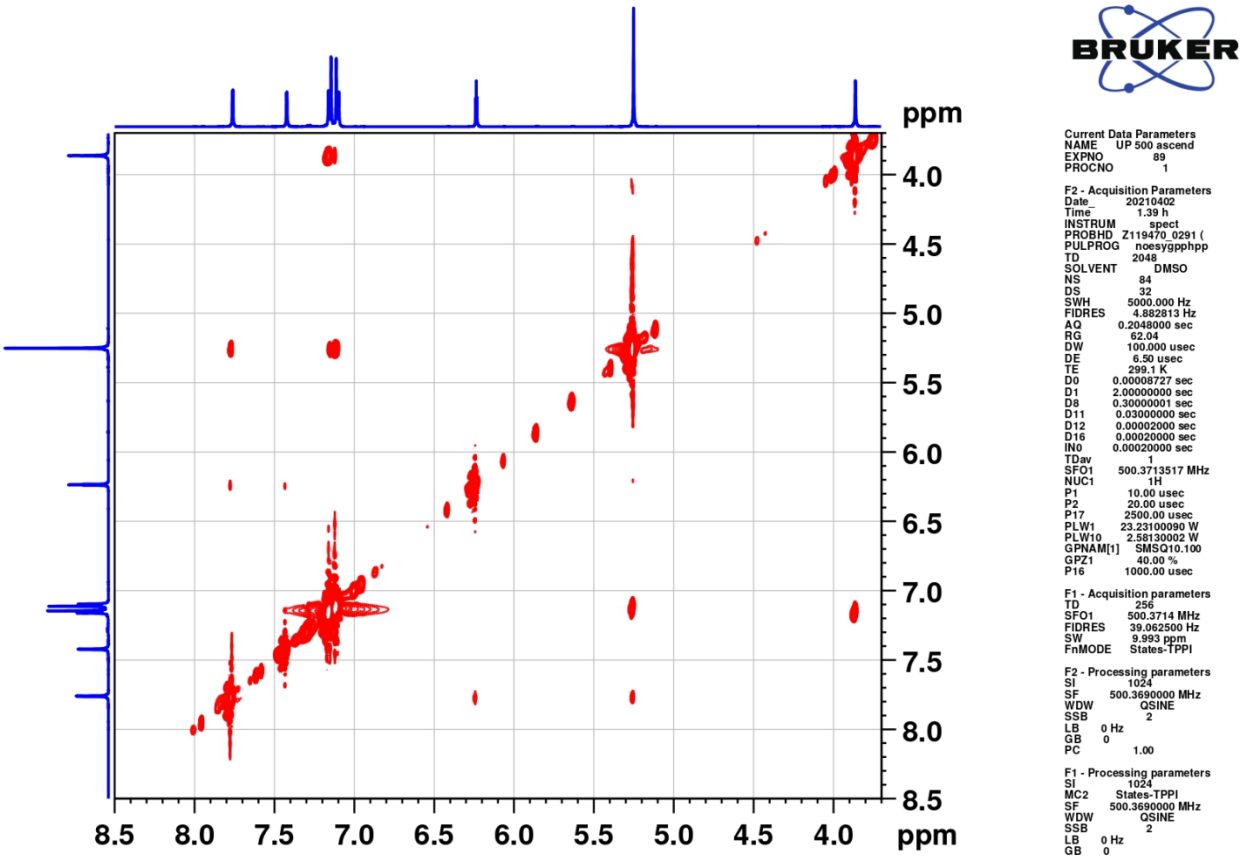

Figure S3. ^{1}H–^{1}H NOESY NMR spectrum of L^{1} in DMSO–d_6.

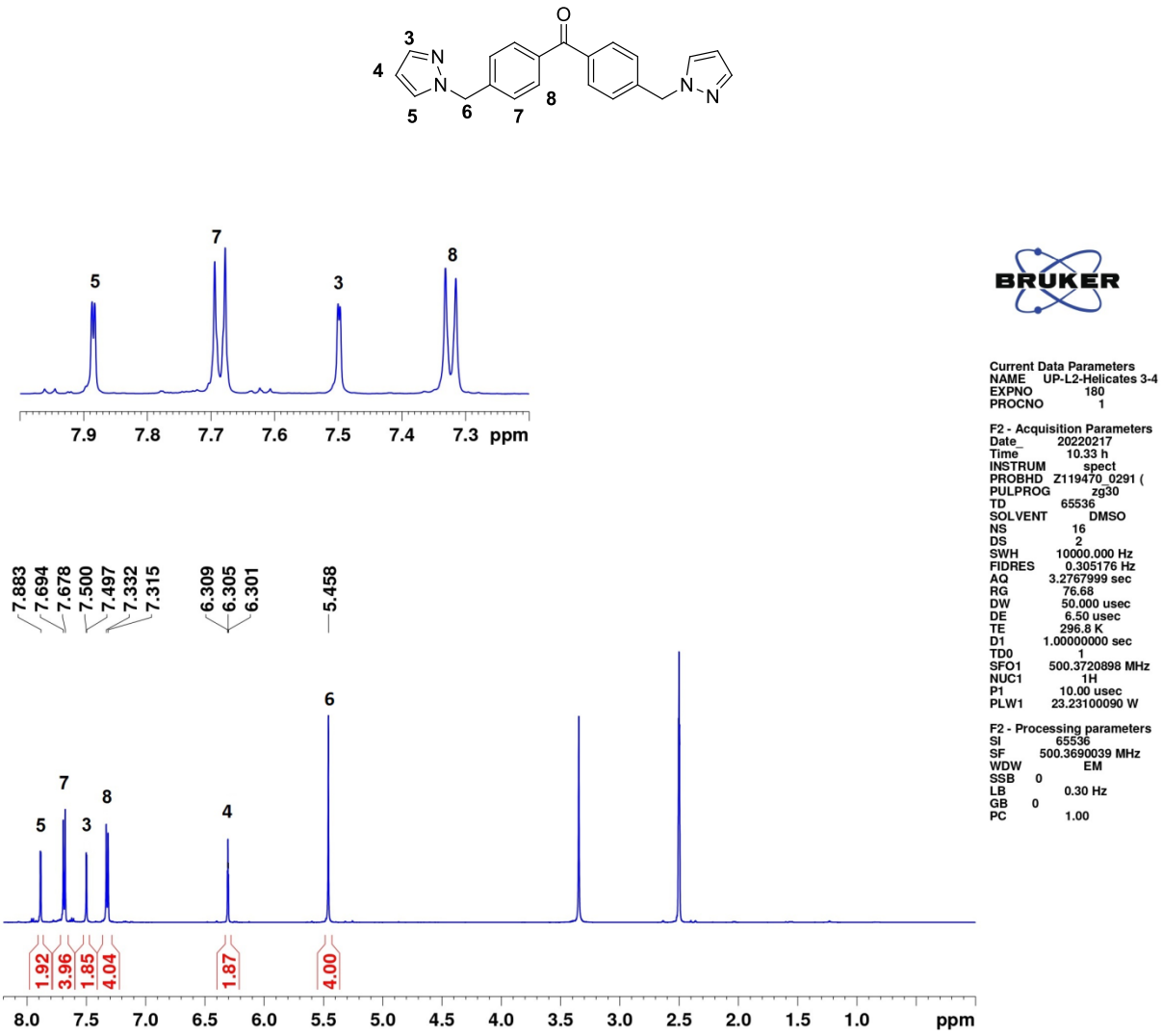

Figure S4. ^{1}H NMR spectrum of L^{2} in DMSO–d_6.

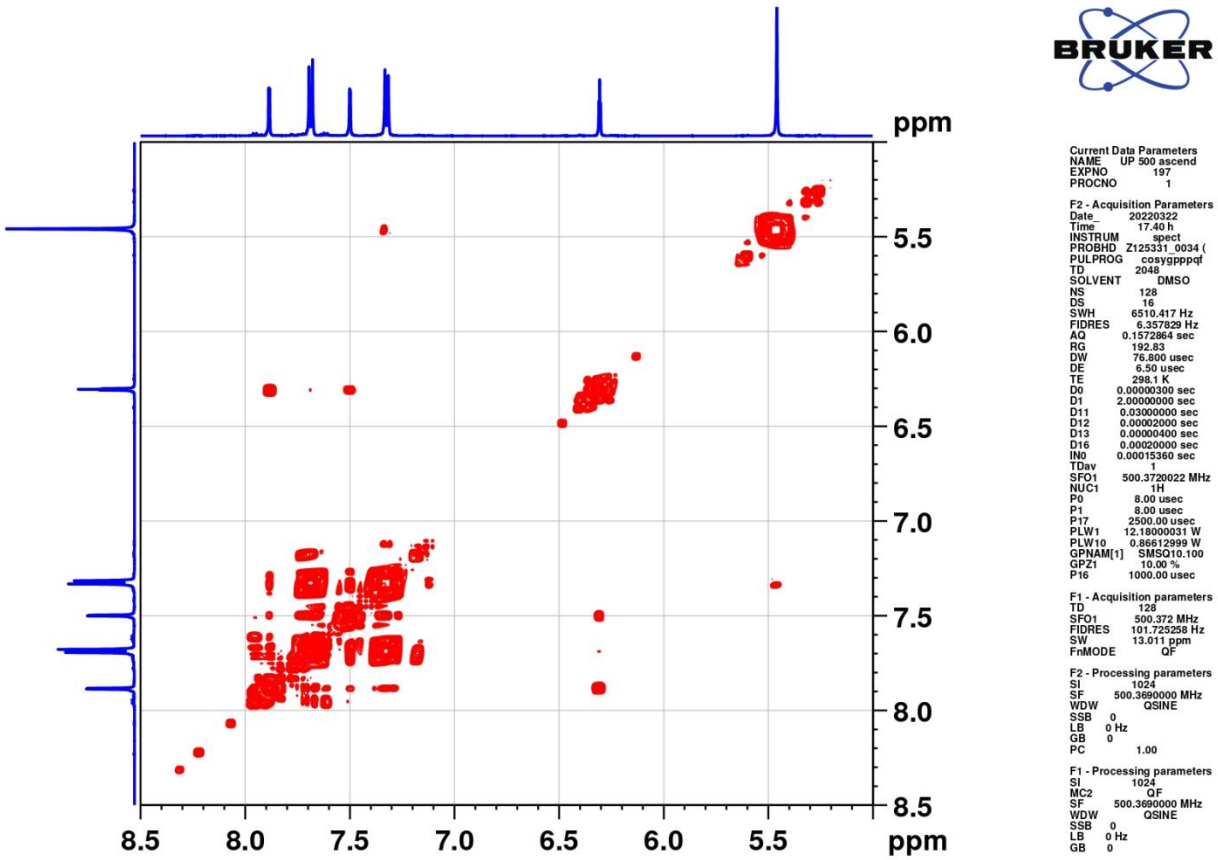

Figure S5. $^{1}H–^{1}H$ COSY NMR spectrum of L^{2} in DMSO–d_6.

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C

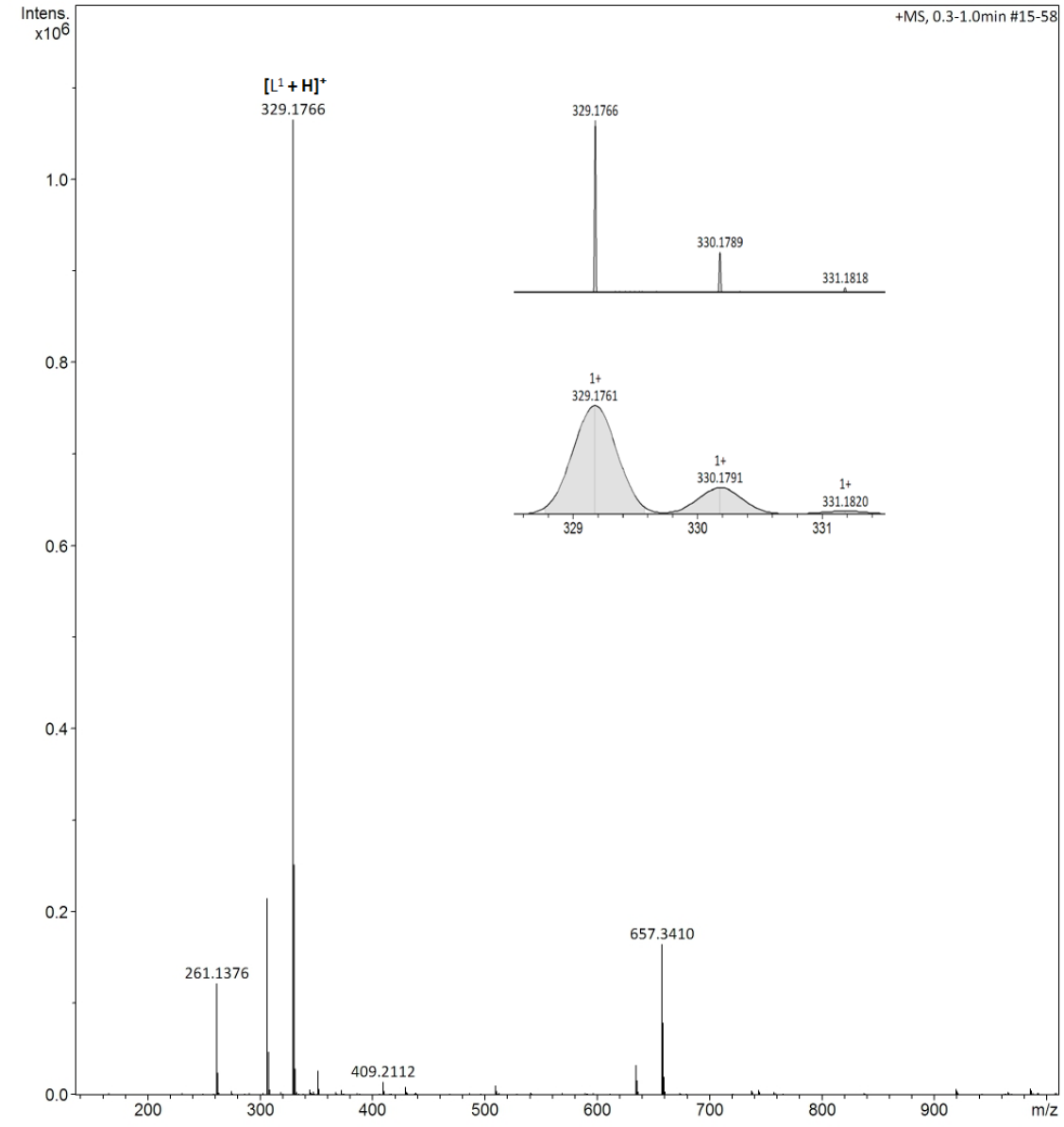

Figure S6. ESI mass spectrum of L^1 in positive ion mode (simulated pattern in inset).

Acquisition Parameter

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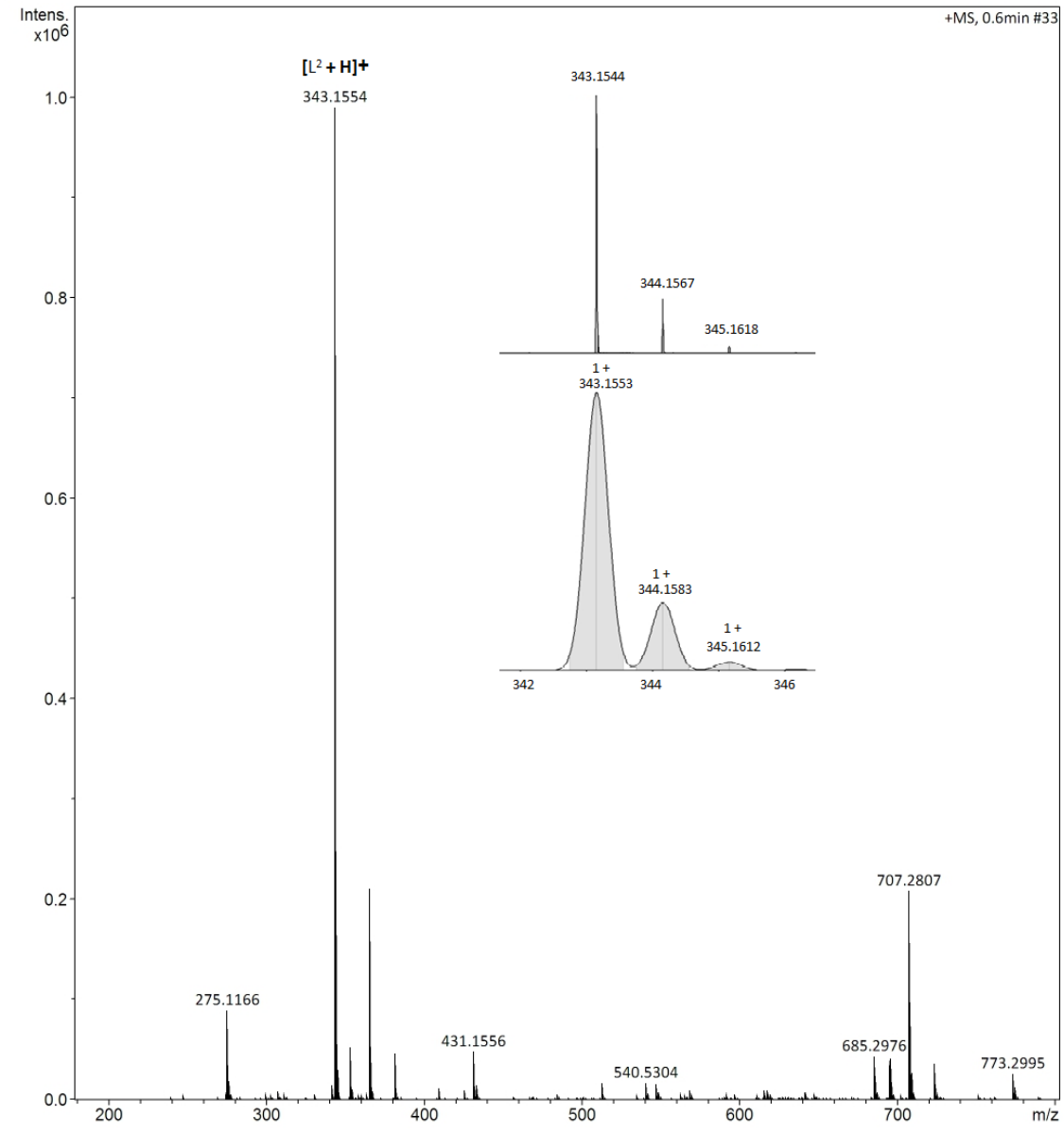


Figure S7. ESI mass spectrum of L^2 in positive ion mode (simulated pattern in inset).

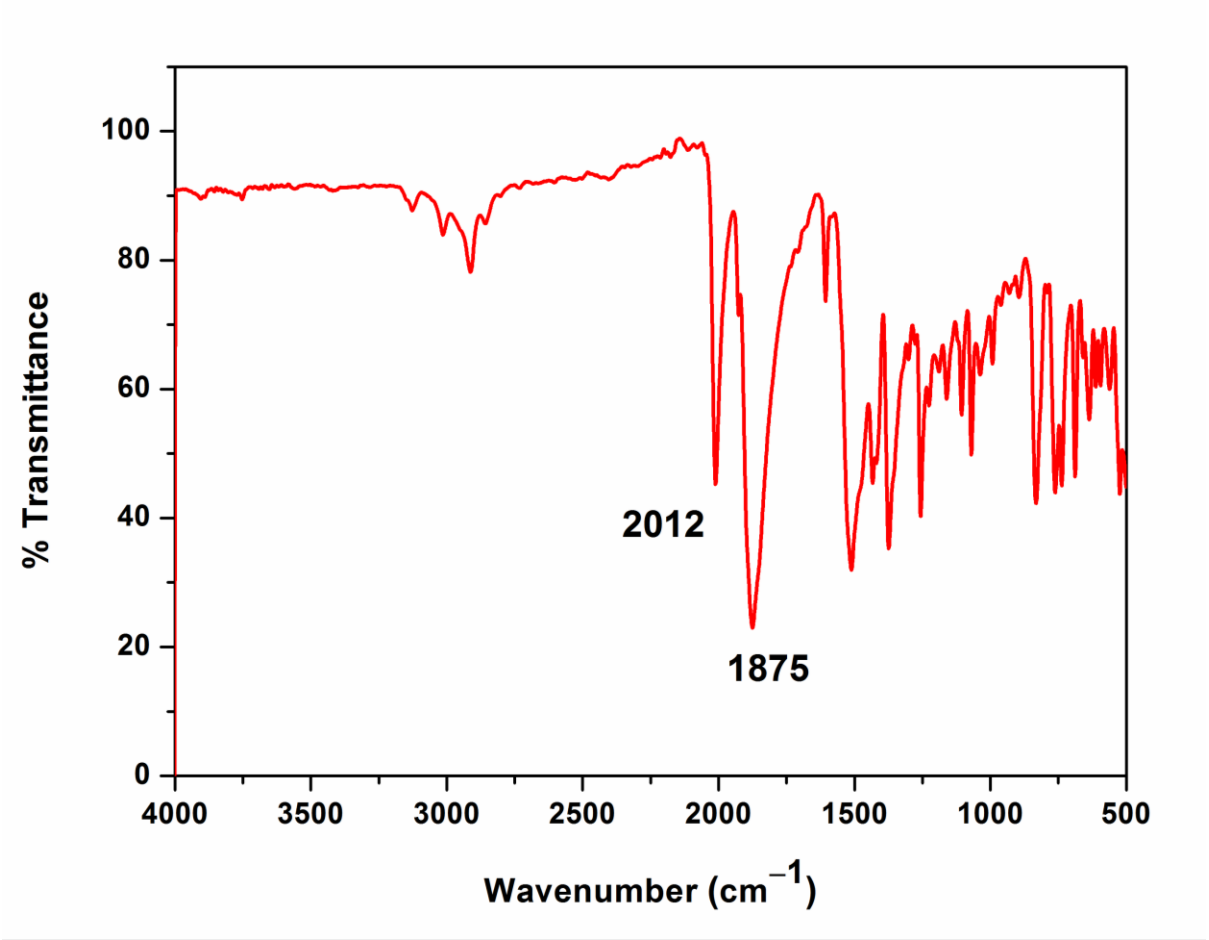


Figure S8. ATR–IR spectrum of **1**.

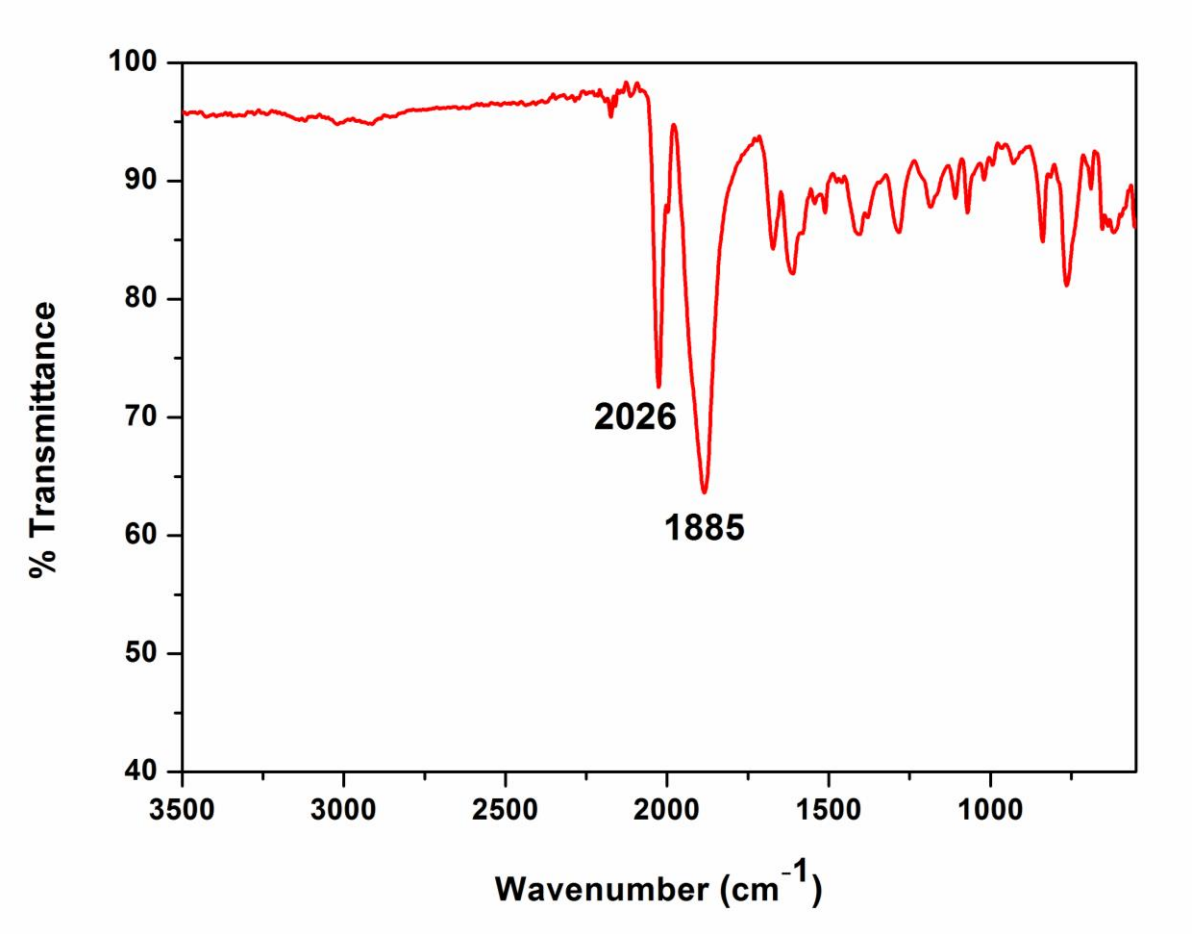


Figure S9. ATR–IR spectrum of **2**.

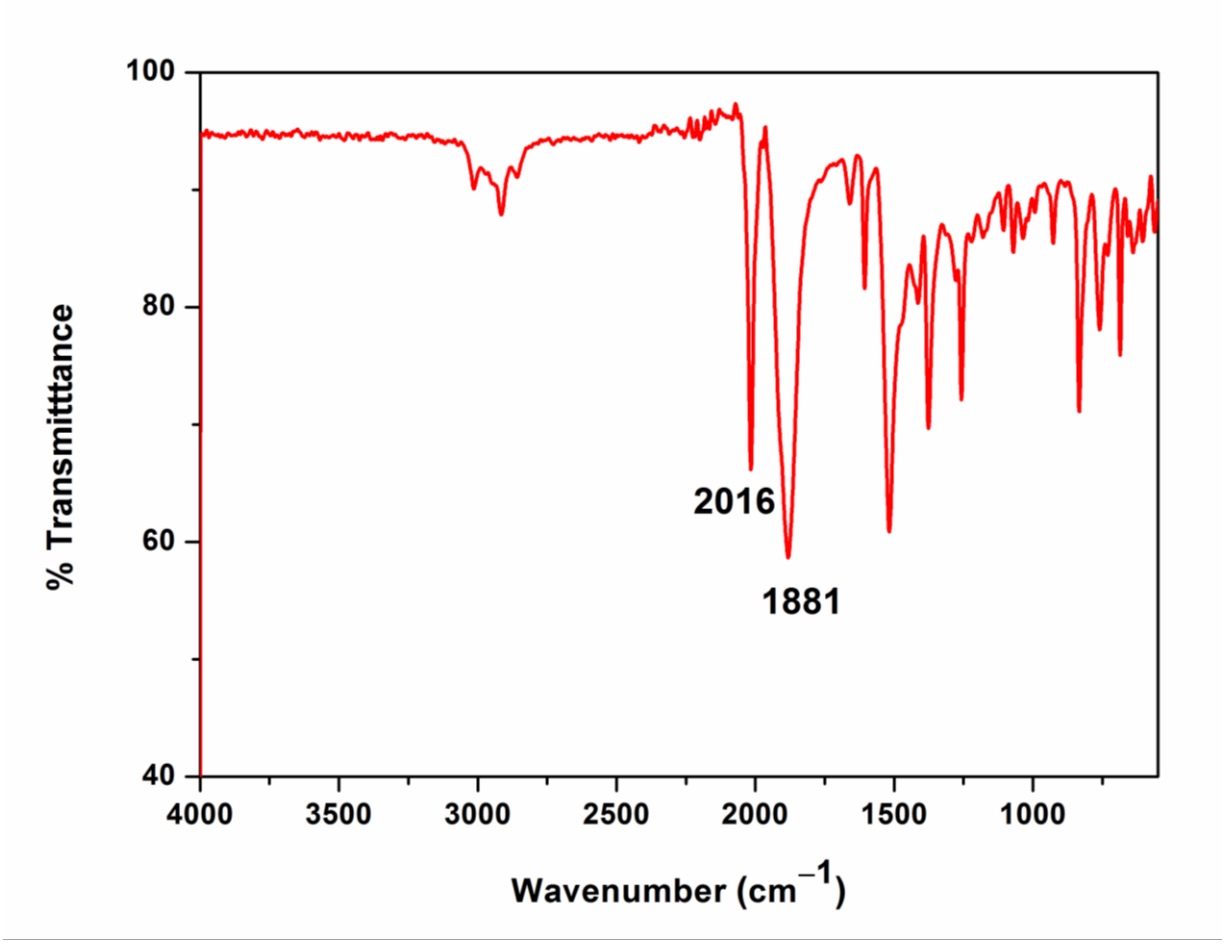


Figure S10. ATR–IR spectrum of **3**.

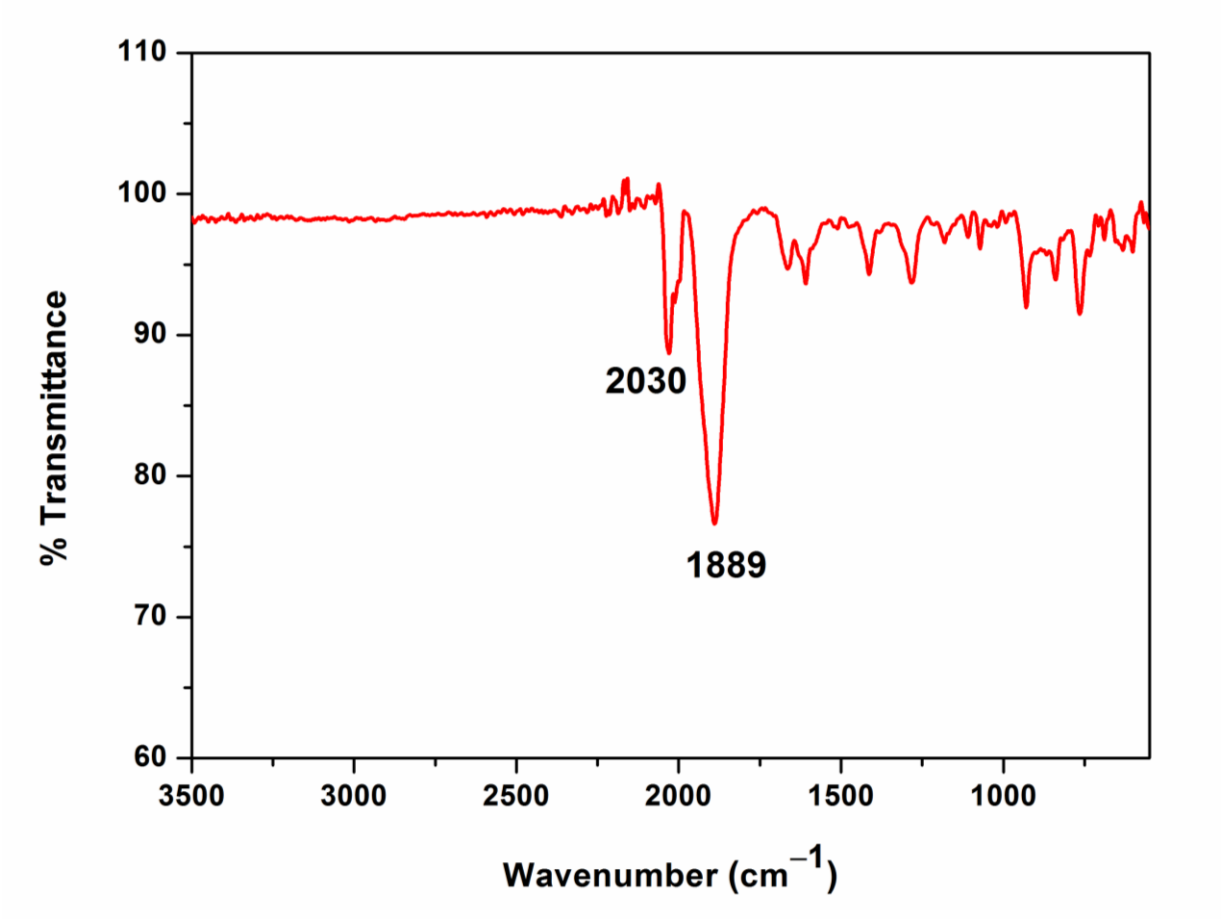


Figure S11. ATR–IR spectrum of **4**.

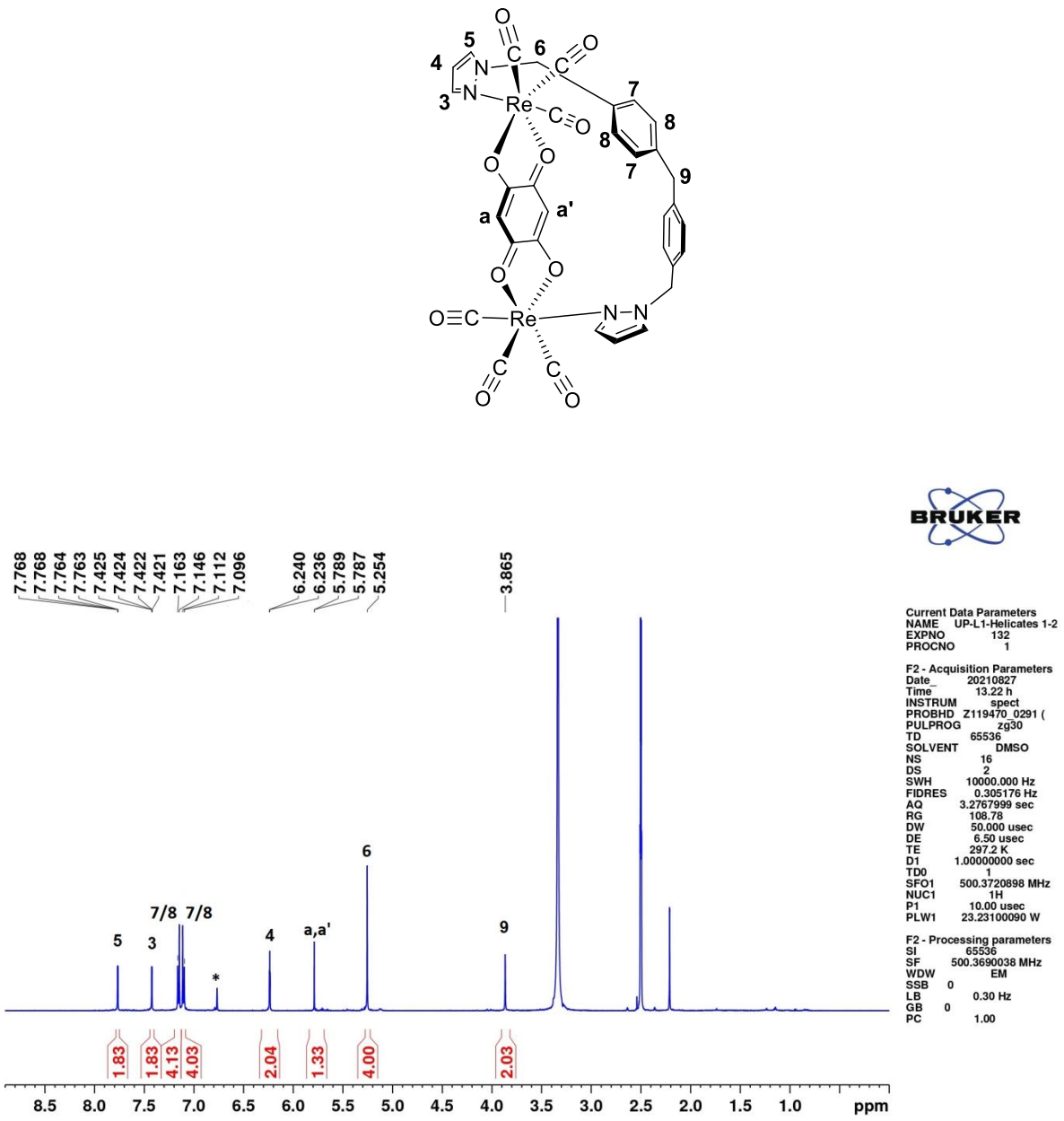


Figure S12. ^{1}H NMR spectrum of **1** in DMSO–d_6 (* = Mesitylene).

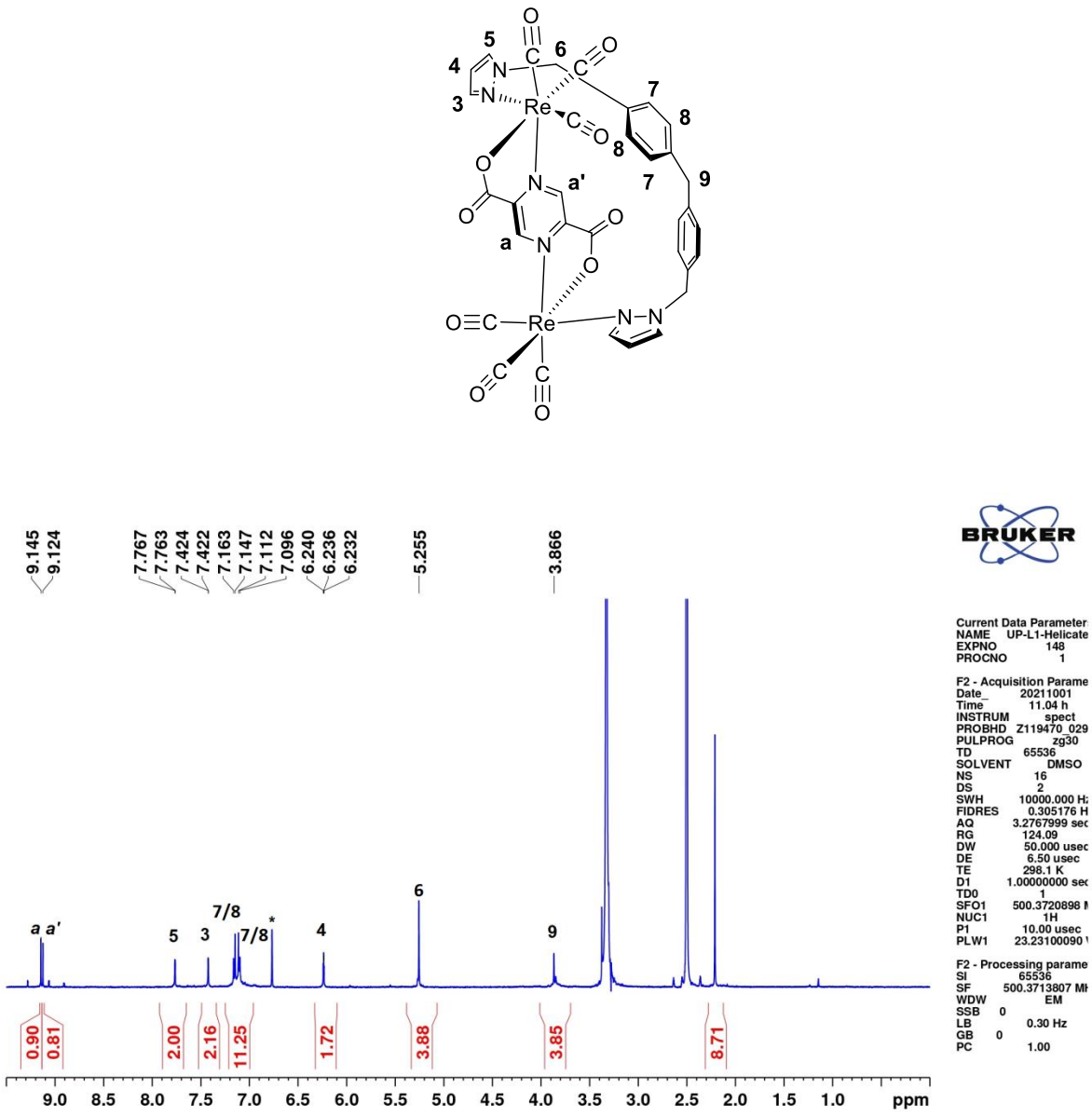


Figure S13. ^{1}H NMR spectrum of **2** in DMSO–d_6 (* = Mesitylene).

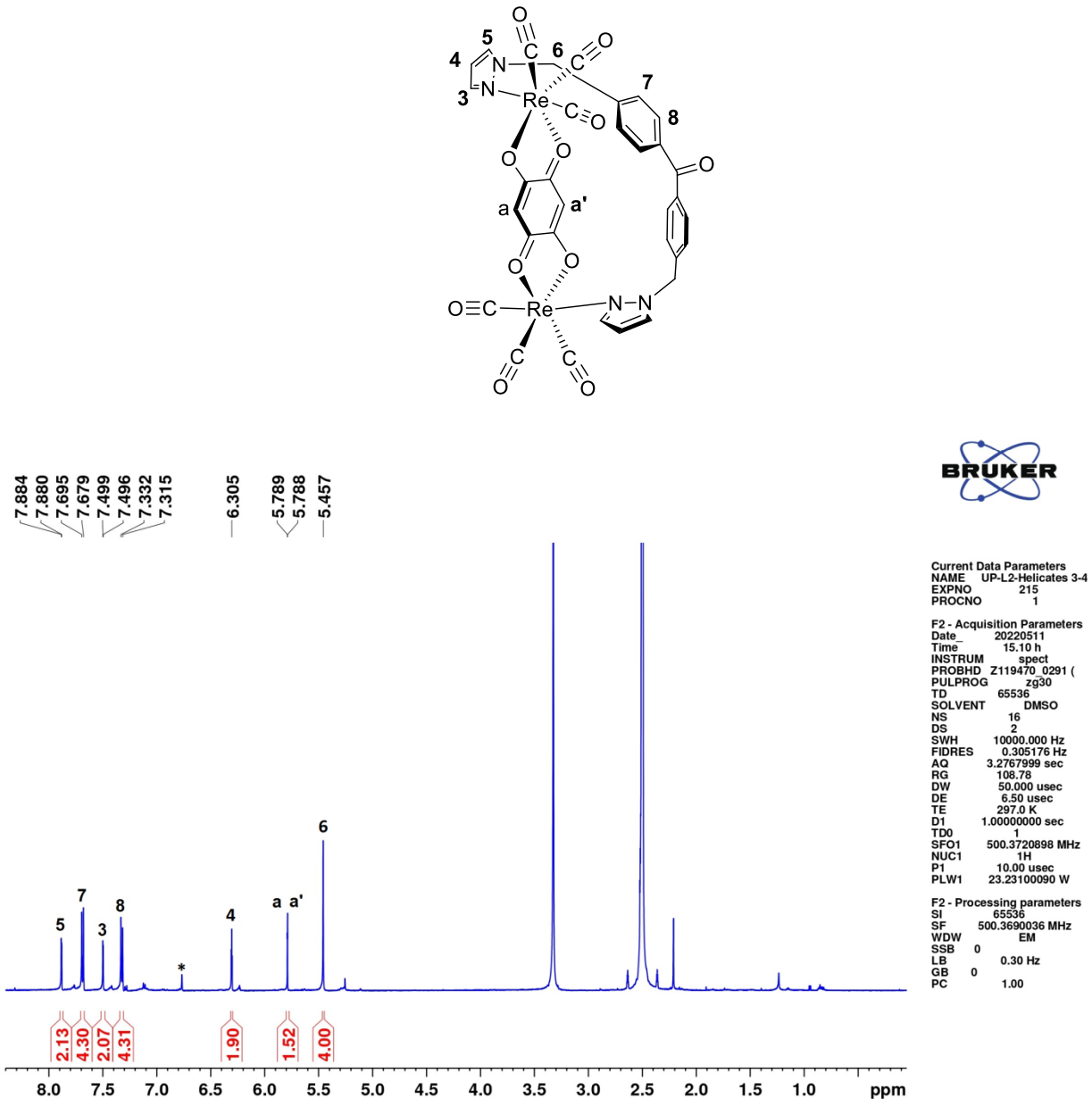


Figure S14. ^{1}H NMR spectrum of **3** in DMSO–d_6 (* = Mesitylene).

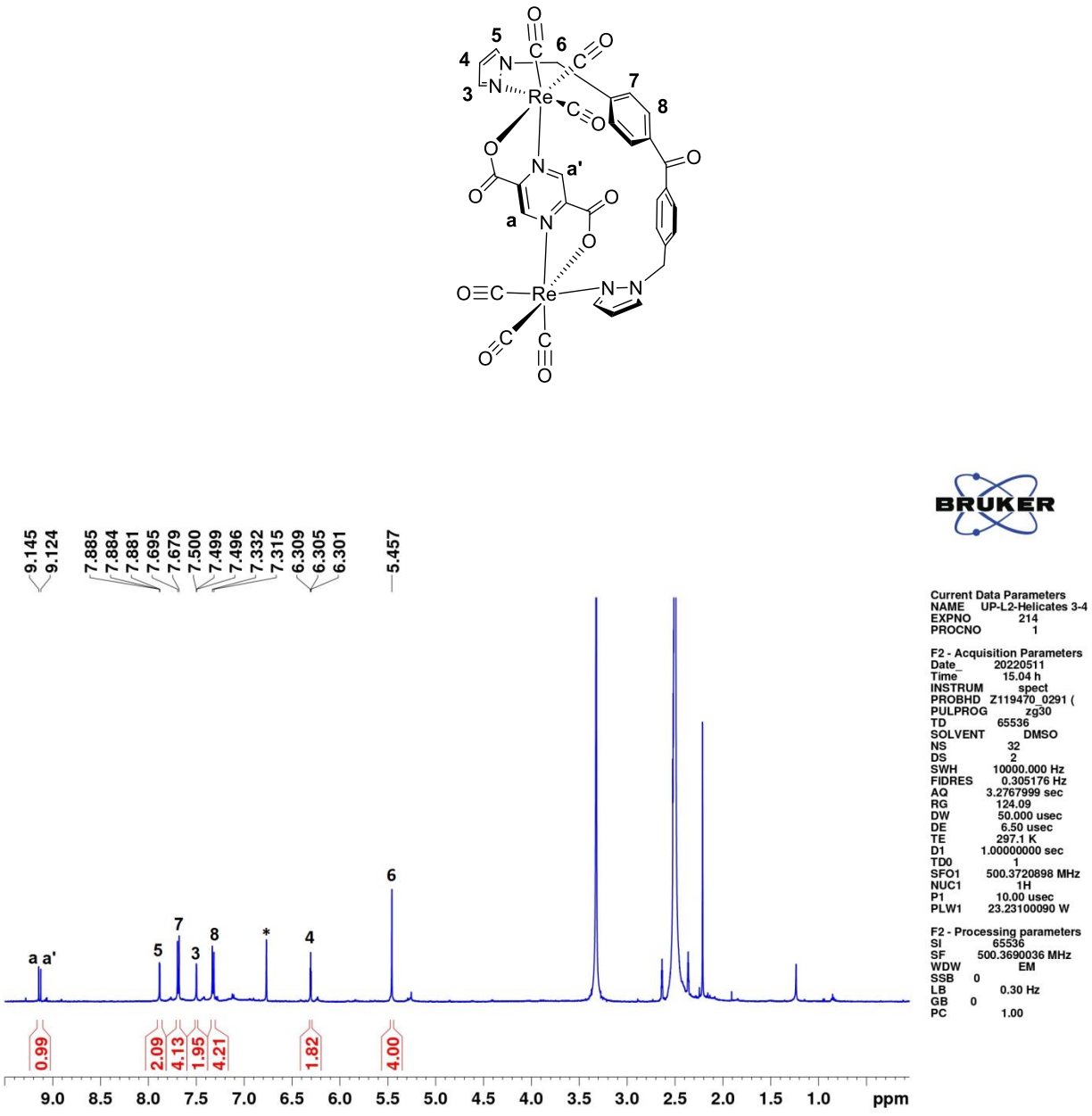


Figure S15. ^{1}H NMR spectrum of **4** in DMSO–d_6 (* = Mesitylene).

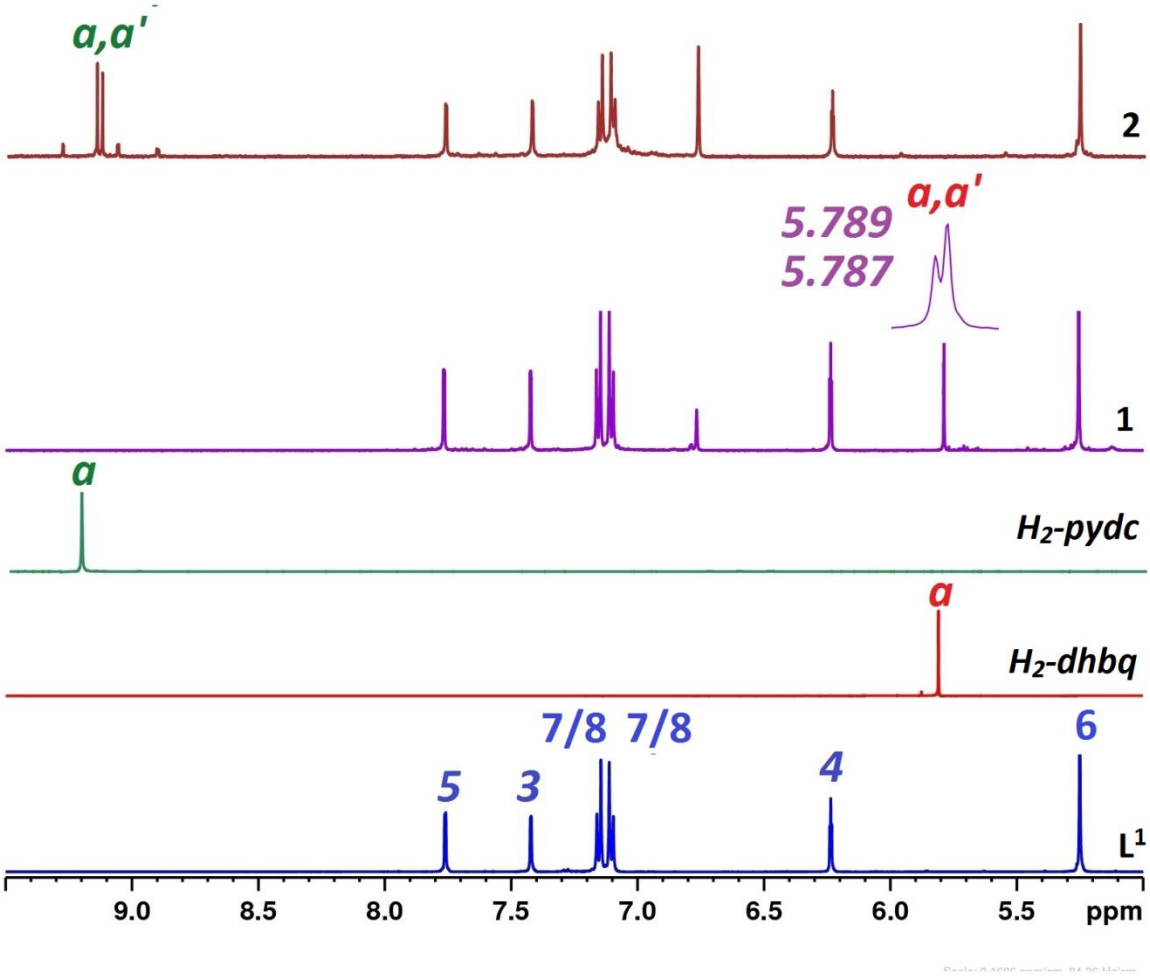


Figure S16. Partial ^{1}H NMR spectra of ligands and complexes **1** and **2** in DMSO–d_6.

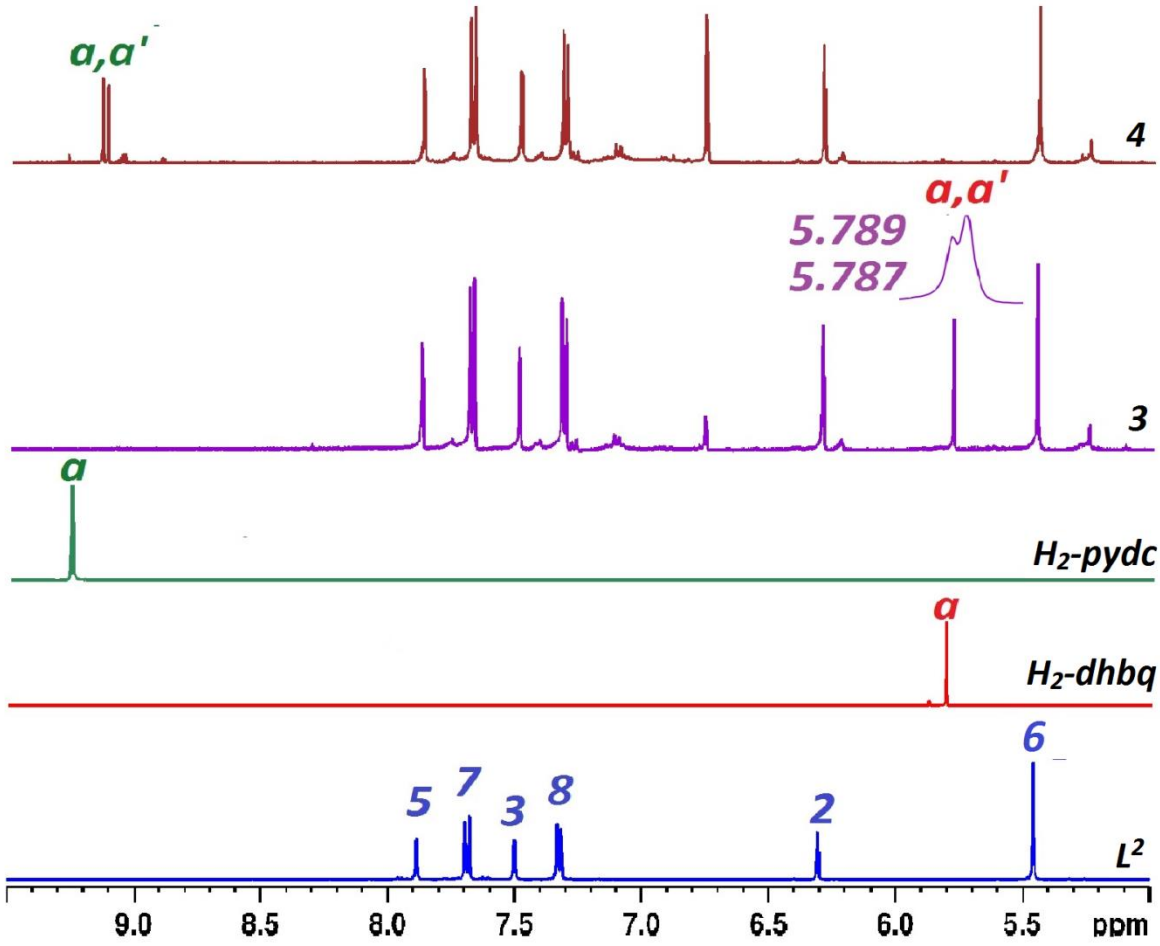


Figure S17. Partial ^{1}H NMR spectra of ligands and complexes **3** and **4** in DMSO–d_6.

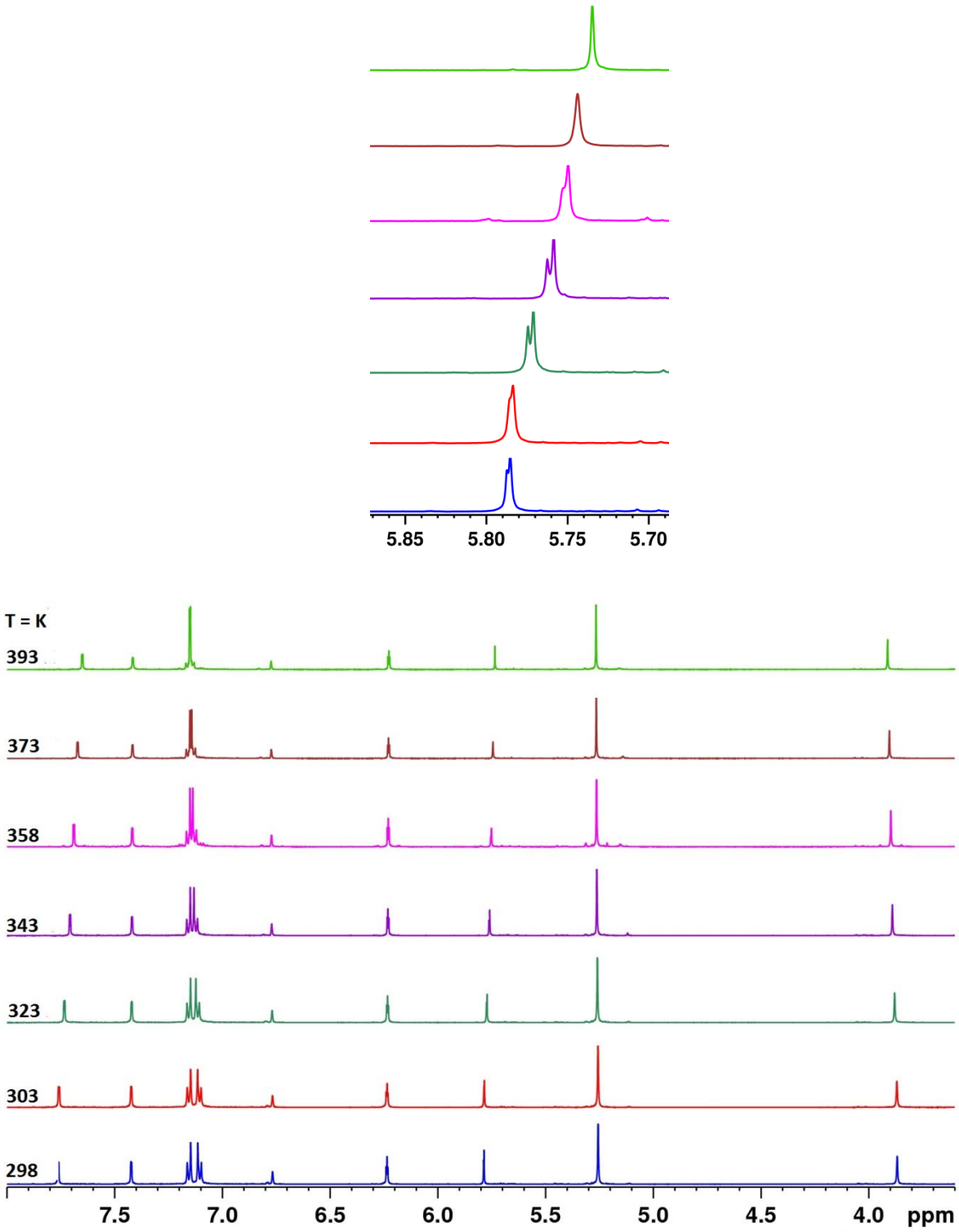


Figure S18. Partial variable temperature ^{1}H NMR spectrum of **1** in DMSO–d_6.

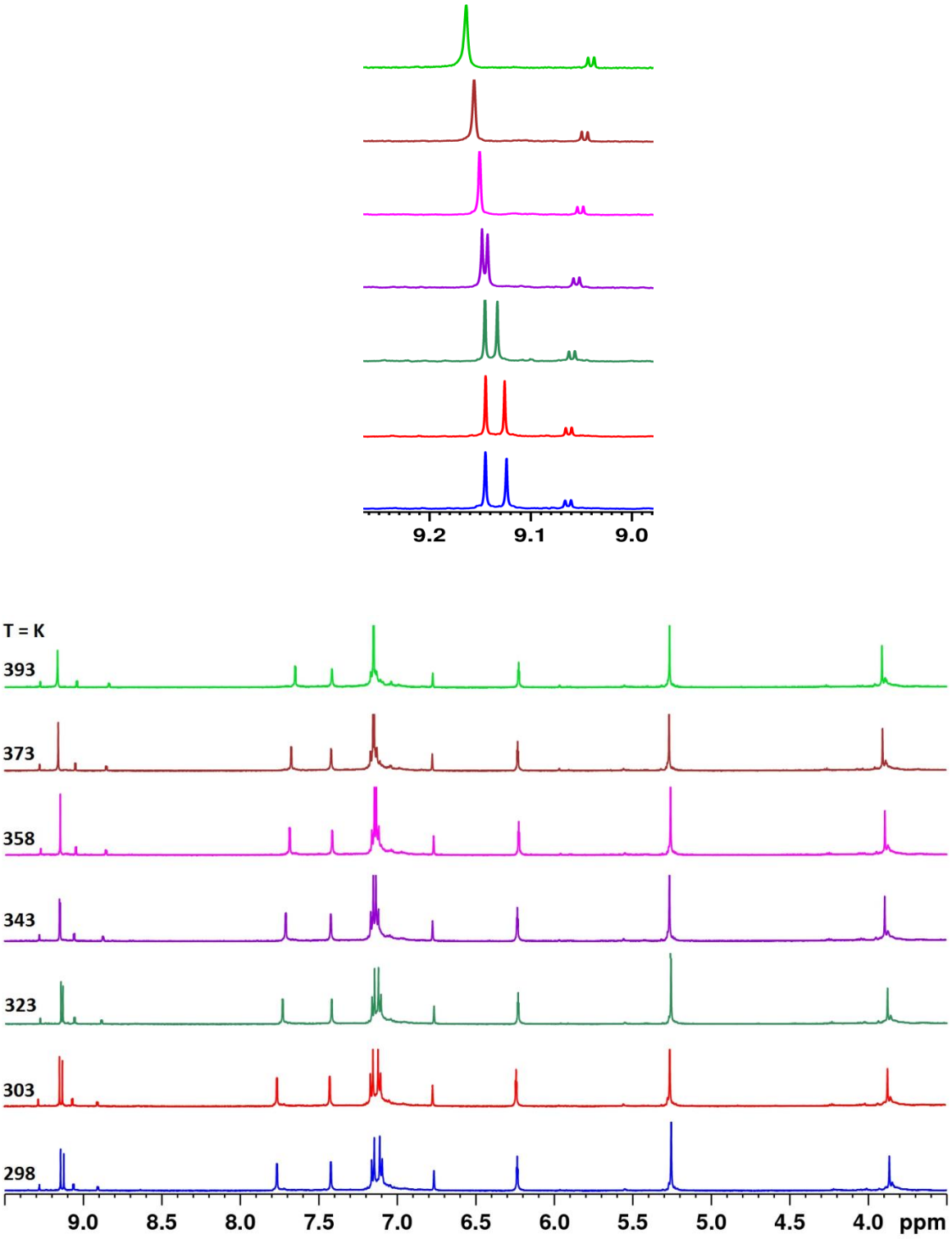


Figure S19. Partial variable temperature ^{1}H NMR spectrum of **2** in DMSO–d_6.

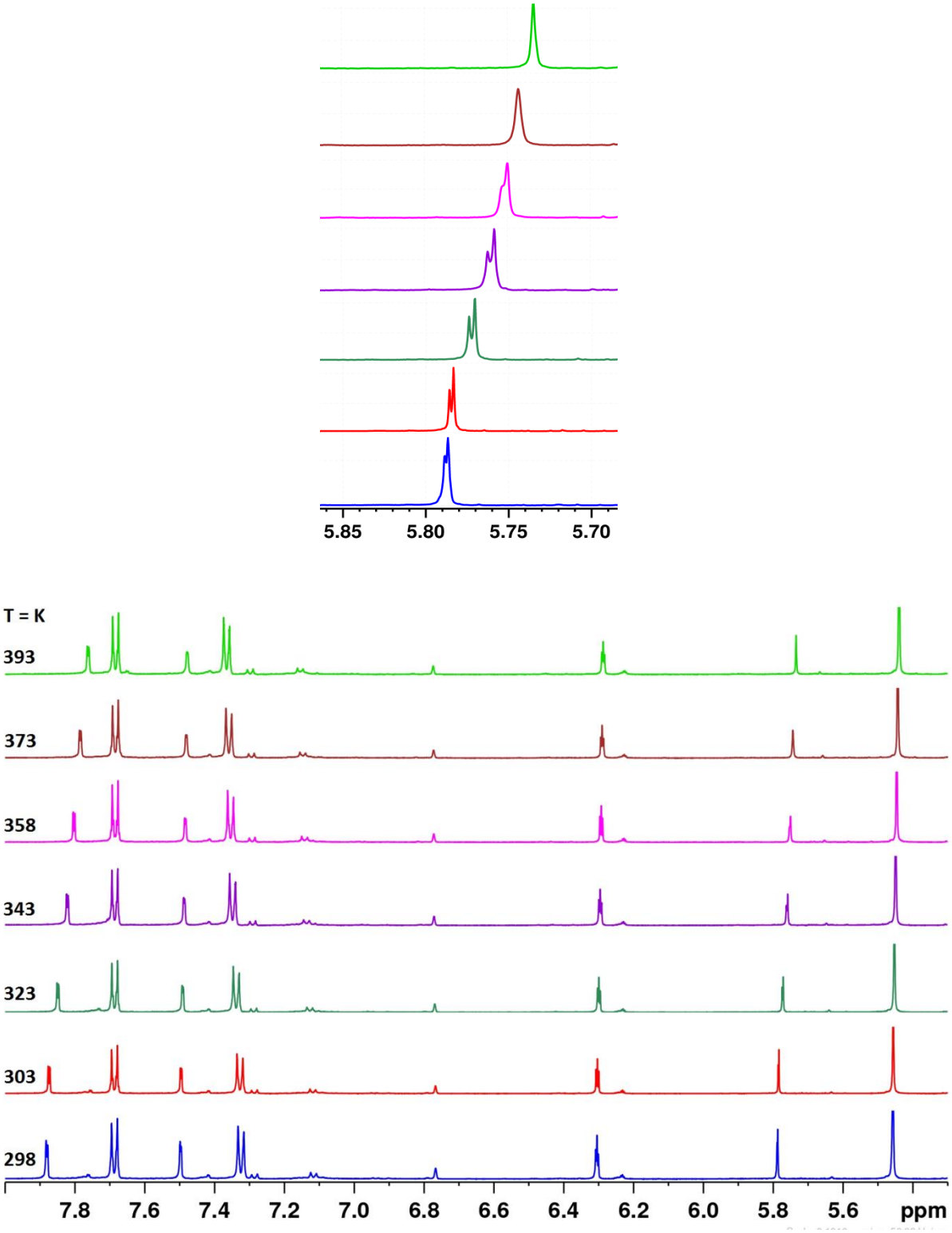


Figure S20. Partial variable temperature ^{1}H NMR spectrum of **3** in DMSO–d_6.

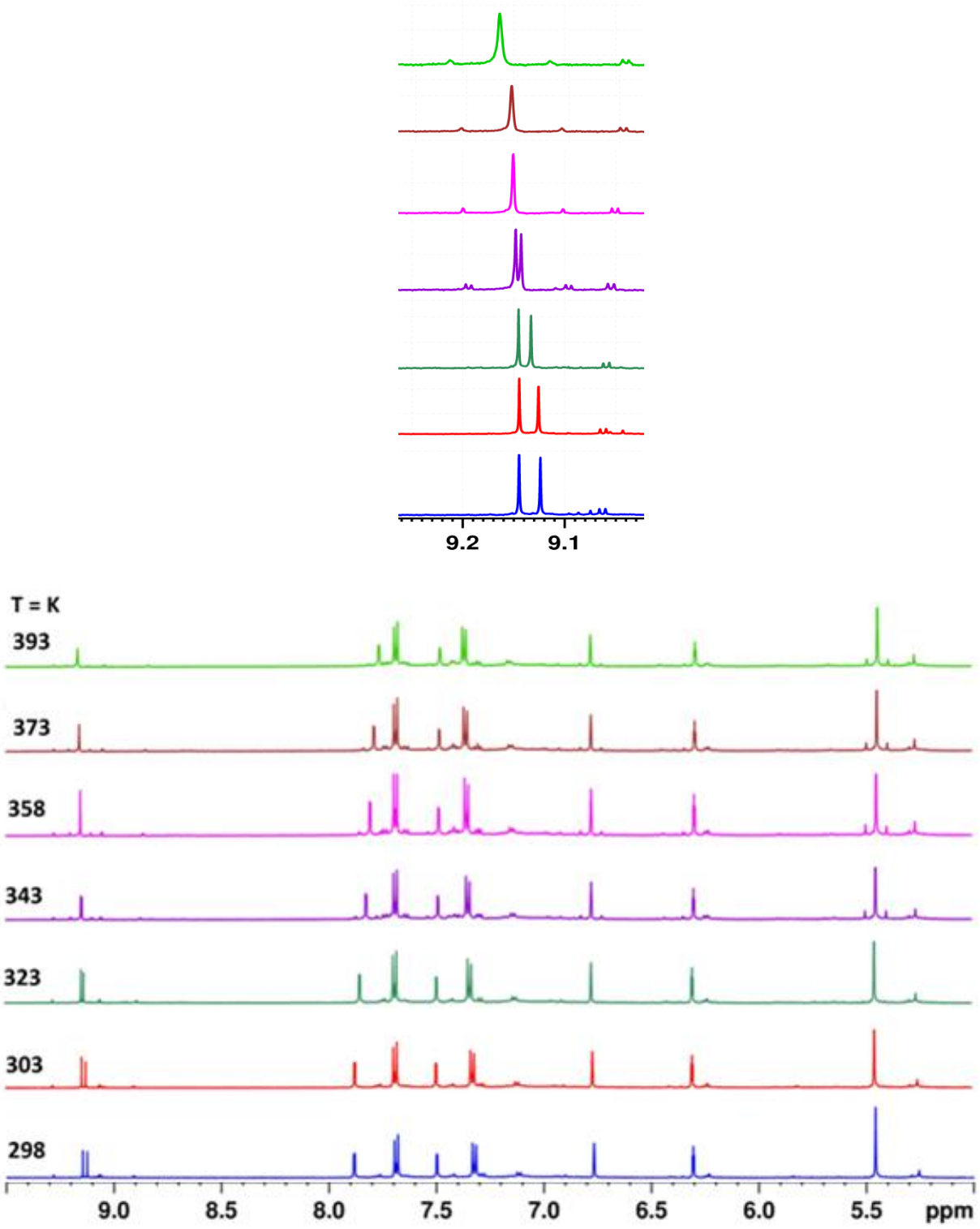


Figure S21. Partial variable temperature ^{1}H NMR spectrum of **4** in DMSO–d_6.

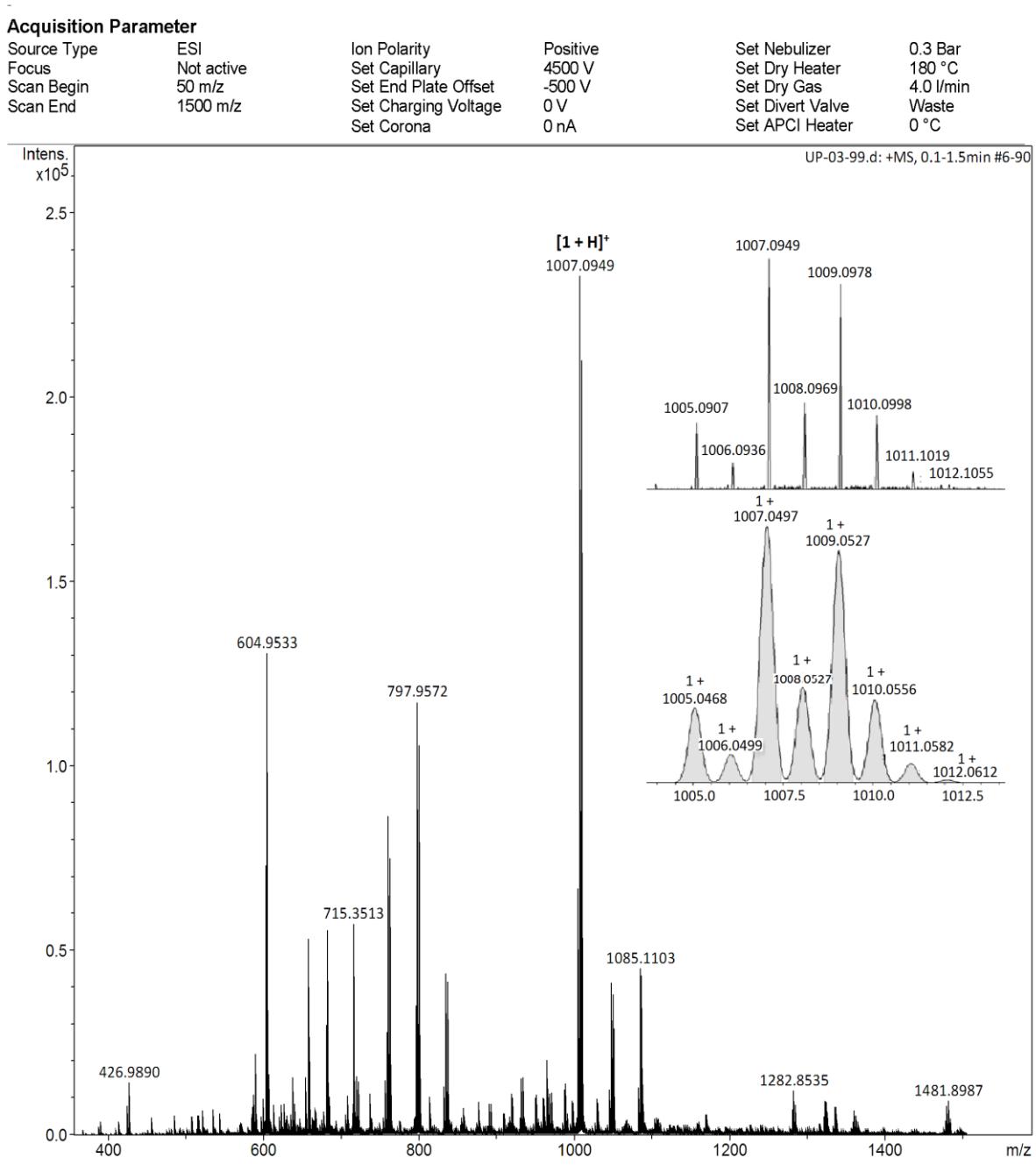


Figure S22. ESI mass spectrum of **1** in positive ion mode (simulated pattern in inset).

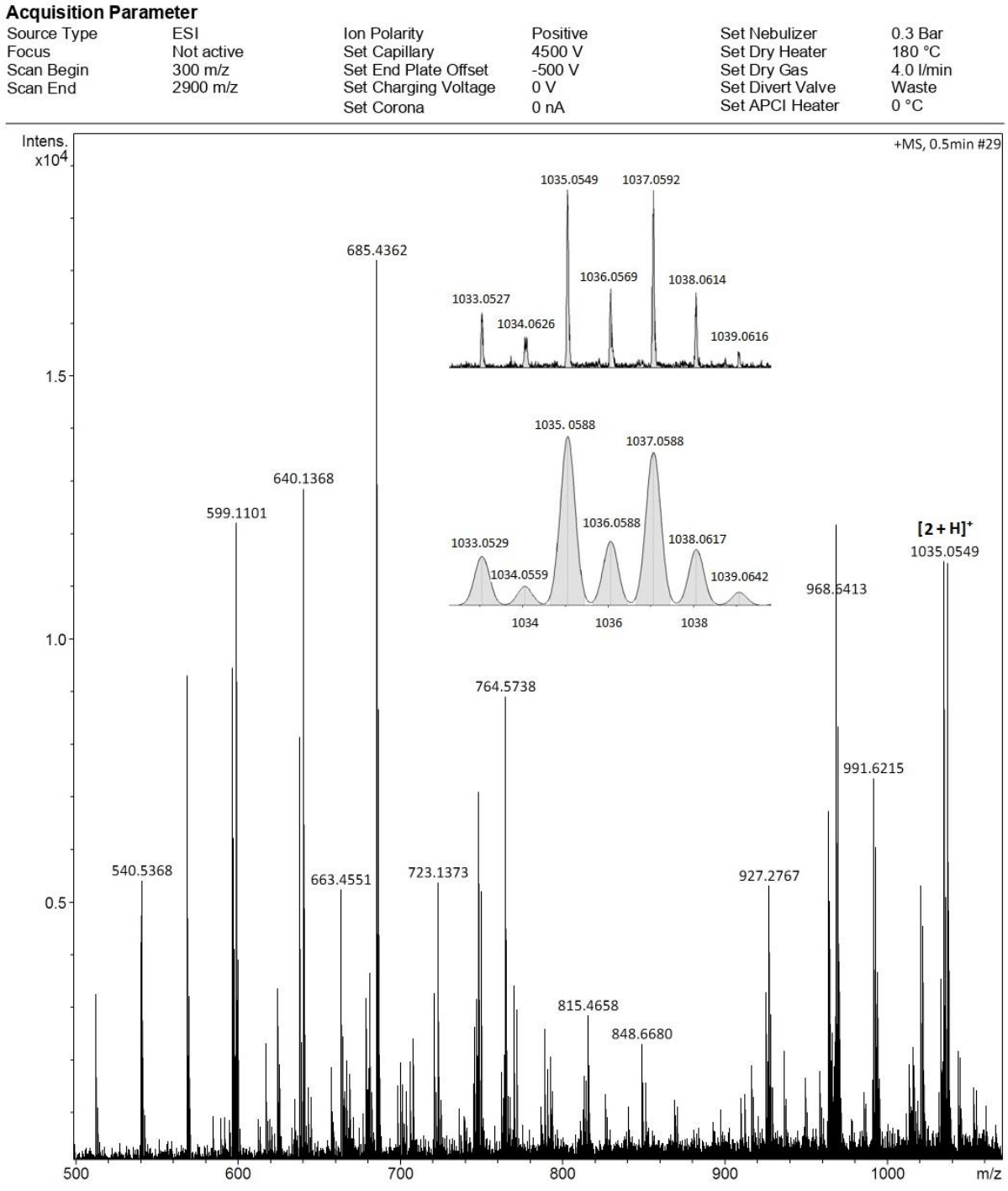


Figure S23. ESI mass spectrum of **2** in positive ion mode (simulated pattern in inset).

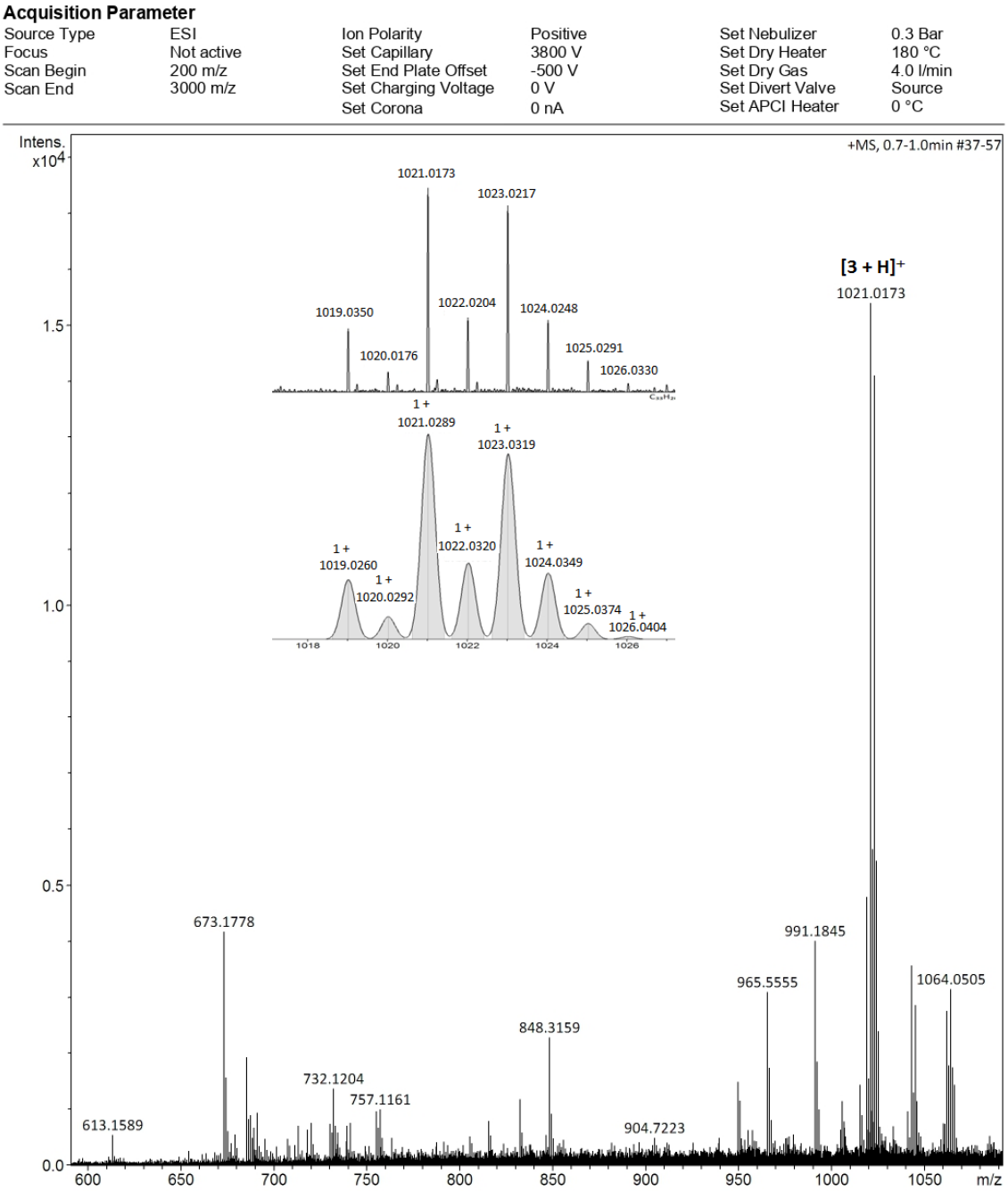


Figure S24. ESI mass spectrum of **3** in positive ion mode (simulated pattern in inset).

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

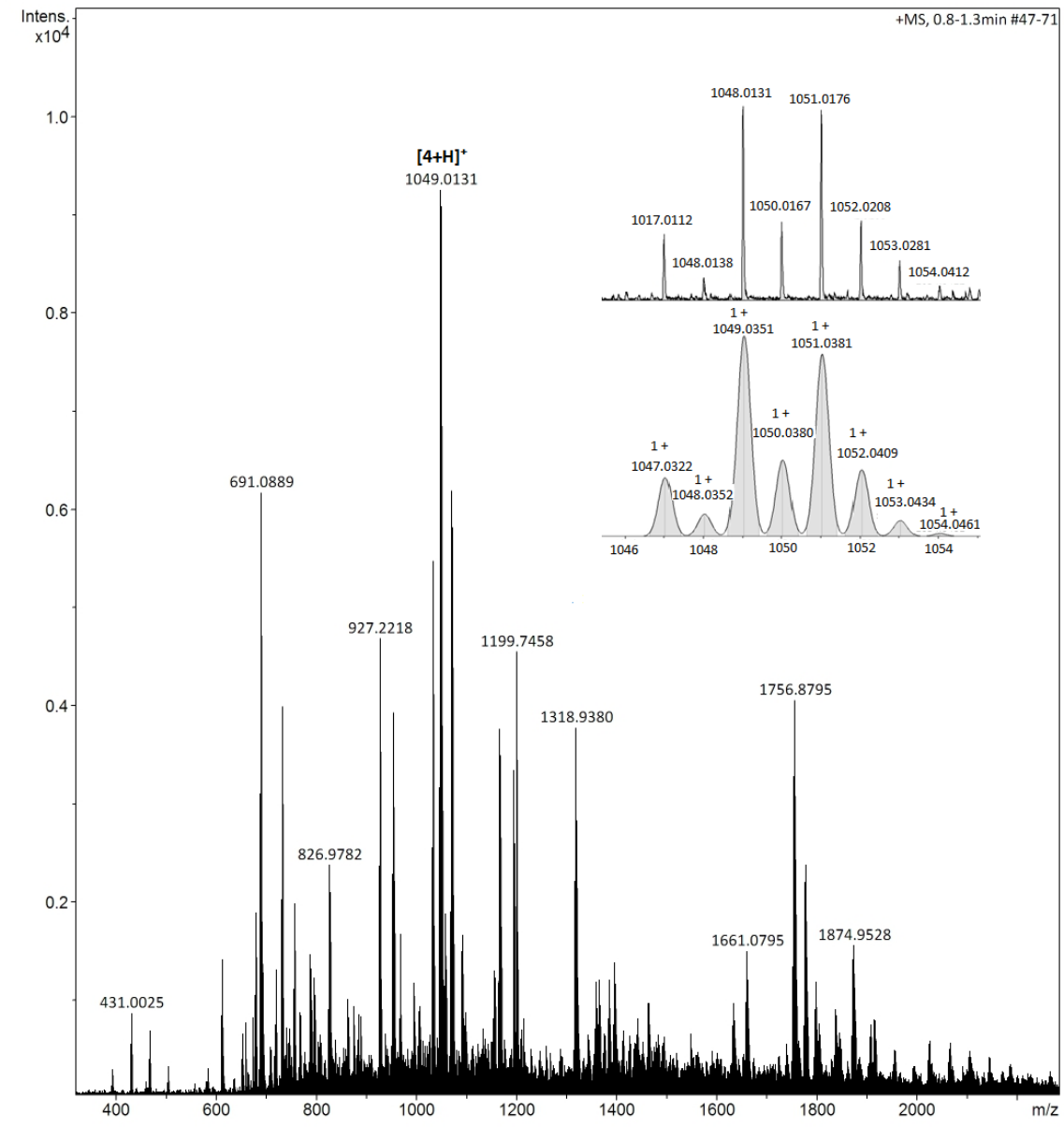
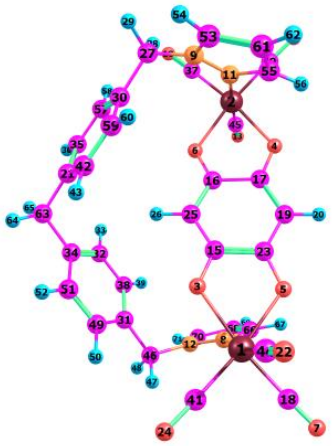


Figure S25. ESI mass spectrum of **4** in positive ion mode (simulated pattern in inset).

Cartesian coordinates of the optimized structure of 1 (Helicate)



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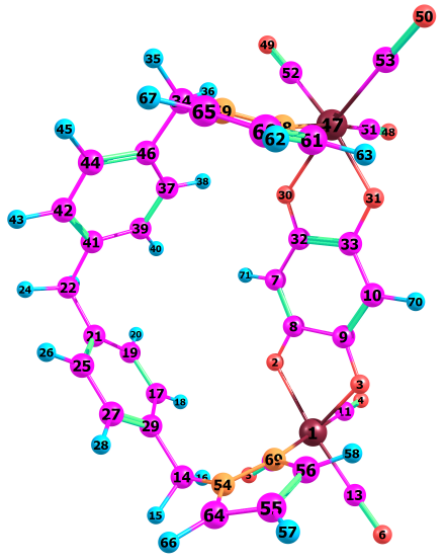
Cartesian coordinates of the optimized structure of 1(Mesocate)



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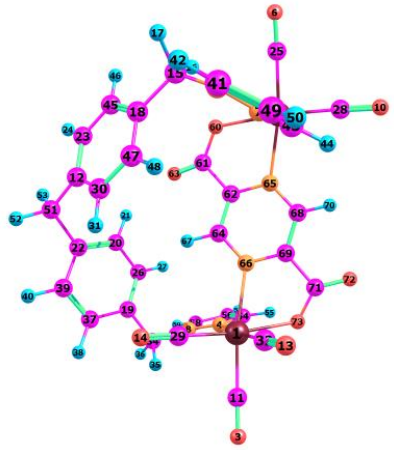
1	-3.107272000	-1.261152000	2.827989000
7	4.117091000	1.697115000	1.401533000
6	3.516427000	1.175295000	3.466029000
6	3.503022000	0.046437000	2.641293000
1	3.280942000	1.229488000	4.516447000
1	3.257952000	-0.975674000	2.880976000
6	-4.321436000	1.758115000	2.942018000
6	3.909582000	2.205303000	2.636600000
1	-4.674864000	2.727559000	3.255750000
1	4.048117000	3.257317000	2.827850000
7	3.864849000	0.358597000	1.389457000
7	-3.884556000	0.133551000	1.479197000
1	0.086591000	-2.982466000	1.756562000
1	0.072310000	0.376996000	-2.077114000

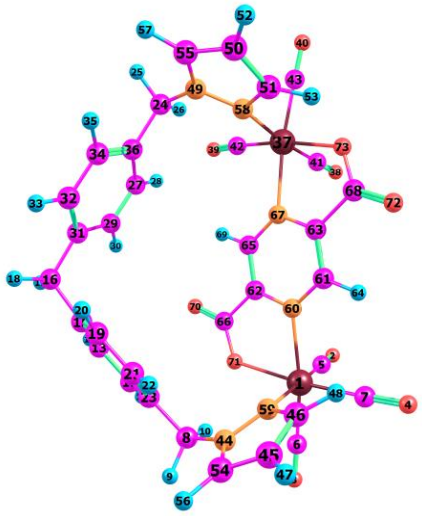
Cartesian coordinates of the optimized structure of 2 (Helicate)



Atom	X	Y	Z
75	-3.193485000	-1.226122000	0.729789000
75	3.806723000	-0.826660000	-0.597093000
8	-6.068612000	-1.985155000	1.589360000
7	-3.878371000	-0.862318000	-1.417272000
7	3.625846000	1.179352000	2.090033000
8	6.748004000	0.136204000	-0.531248000
7	3.414880000	-0.049620000	1.536693000
7	-4.551406000	0.175536000	-1.996025000
8	4.184596000	-1.850714000	-3.487165000
8	4.622601000	-3.593038000	0.505270000
6	-4.999464000	-1.690477000	1.284399000
6	0.289142000	4.704774000	0.333305000
8	-2.132920000	-2.047239000	3.512442000
8	-3.464153000	1.551469000	2.035748000
6	3.844082000	2.404403000	1.317920000
1	4.299557000	2.120920000	0.371991000
1	4.580600000	2.989626000	1.876052000
6	2.589246000	3.222603000	1.049101000
6	-4.001951000	2.475009000	-1.109481000
6	-1.836676000	3.483917000	-1.516435000
1	-0.873710000	3.436274000	-2.010511000
6	-2.074787000	4.459014000	-0.541990000
6	1.528516000	4.966749000	-0.254867000
1	1.604773000	5.719474000	-1.033688000
6	5.660228000	-0.239430000	-0.553474000
6	-2.787909000	2.505294000	-1.796687000
1	-2.554425000	1.741301000	-2.531399000
6	4.343893000	-2.552997000	0.084998000
6	-3.409372000	0.539723000	1.476142000
6	0.233013000	3.719866000	1.323127000
1	-0.714268000	3.491346000	1.802447000
6	-2.531179000	-1.739662000	2.477558000
6	4.047207000	-1.472482000	-2.409784000
6	-5.020107000	1.359584000	-1.277770000
1	-5.382285000	1.027003000	-0.304477000
1	-5.895036000	1.712607000	-1.830248000

6	-4.274363000	3.493291000	-0.194782000
1	-5.212585000	3.494476000	0.352896000
6	-3.323501000	4.470396000	0.084151000
1	-3.542576000	5.222569000	0.836419000
6	3.482635000	1.124262000	3.433278000
1	3.603445000	2.013414000	4.032319000
6	3.140443000	-0.863282000	2.565604000
1	2.959404000	-1.911469000	2.388825000
6	2.659976000	4.238166000	0.094601000
1	3.595340000	4.429191000	-0.423287000
6	1.364637000	2.987255000	1.676369000
1	1.270635000	2.210165000	2.427723000
6	3.169031000	-0.173931000	3.781367000
1	2.995835000	-0.568788000	4.769069000
6	-0.971706000	5.421315000	-0.130879000
1	-1.344572000	6.076062000	0.664490000
1	-0.717078000	6.078030000	-0.969303000
6	-3.684364000	-1.757761000	-2.394295000
1	-3.204987000	-2.693524000	-2.156858000
6	-4.213996000	-1.303556000	-3.606826000
1	-4.210848000	-1.809602000	-4.558379000
6	-4.758122000	-0.071742000	-3.310184000
1	-5.277788000	0.645276000	-3.926410000
8	2.963891000	1.055857000	-1.264181000
6	1.684126000	1.180859000	-1.339474000
6	0.916843000	0.000353000	-0.762311000
8	1.047779000	2.084742000	-1.852287000
6	-0.434960000	0.071339000	-0.446924000
7	1.598894000	-1.151437000	-0.607640000
7	-1.116359000	-1.023478000	-0.088302000
1	-0.954004000	1.019686000	-0.474752000
6	0.888543000	-2.268016000	-0.375674000
6	-0.482151000	-2.212623000	-0.167463000
1	1.402140000	-3.220138000	-0.348454000
6	-1.350078000	-3.467758000	-0.099213000
8	-0.812398000	-4.552024000	-0.213342000
8	-2.613296000	-3.203632000	-0.005784000

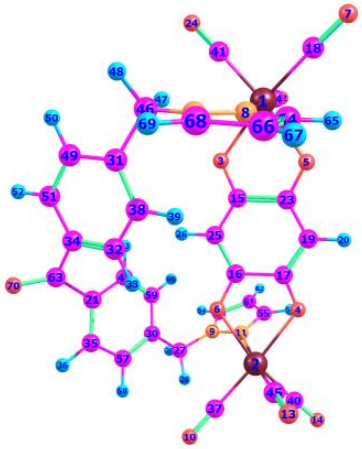
Cartesian coordinates of the optimized structure of 2 (Mesocate).



Atom	X	Y	Z
75	-3.574013000	-1.358657000	-0.256007000
8	-3.136706000	-3.416563000	-2.519024000
8	-6.584728000	-1.237881000	-0.966516000
8	-4.074551000	-3.666115000	1.733352000
6	-3.298034000	-2.651972000	-1.675262000
6	-5.468213000	-1.299214000	-0.693302000
6	-3.914342000	-2.803252000	0.980893000
6	-4.703929000	2.157389000	0.175598000
1	-5.655903000	2.688181000	0.268666000
1	-4.781136000	1.485333000	-0.675627000
6	-3.287870000	3.565855000	-1.339786000
1	-3.880959000	3.196216000	-2.169327000
6	-2.224718000	4.426710000	-1.593005000
1	-2.018038000	4.723123000	-2.616481000
6	-1.390675000	4.861329000	-0.562438000
6	-0.146644000	5.685640000	-0.846629000
1	-0.187365000	6.065411000	-1.871413000
1	-0.117350000	6.561074000	-0.190075000
6	-1.679081000	4.442142000	0.738782000
1	-1.045290000	4.761595000	1.560918000
6	-2.744320000	3.587003000	0.997303000
1	-2.917242000	3.261528000	2.017377000
6	-3.552115000	3.124018000	-0.043777000
6	4.617284000	2.372892000	-0.016134000
1	5.508688000	3.000338000	0.062492000
1	4.777406000	1.709150000	-0.859468000
6	2.614789000	3.102087000	-1.383680000
1	2.897376000	2.379760000	-2.141612000
6	1.494999000	3.902785000	-1.591162000
1	0.898030000	3.756441000	-2.485482000
6	1.116500000	4.865066000	-0.651154000
6	1.900973000	5.008192000	0.496936000
1	1.639942000	5.761415000	1.234890000
6	3.014040000	4.201687000	0.711256000
1	3.596184000	4.339156000	1.617404000

6	3.381346000	3.229452000	-0.222255000
75	3.611129000	-1.305024000	-0.283507000
8	3.087991000	-3.770816000	-2.068445000
8	4.106525000	0.273690000	-2.884316000
8	6.605600000	-2.074232000	-0.106327000
6	3.278753000	-2.847201000	-1.411221000
6	3.948944000	-0.299719000	-1.887988000
6	5.496549000	-1.784568000	-0.186927000
7	-4.574761000	1.345049000	1.387254000
6	-4.435883000	0.808827000	3.530035000
6	-3.807861000	-0.150694000	2.730358000
1	-4.540329000	0.809454000	4.602731000
1	-3.335238000	-1.072286000	3.030292000
7	4.605208000	1.559667000	1.206123000
6	4.749443000	1.002836000	3.343008000
6	4.142342000	-0.015612000	2.602824000
1	4.970027000	1.007925000	4.398006000
1	3.808337000	-0.990712000	2.917527000
6	-4.910565000	1.745826000	2.634213000
6	5.029625000	1.985842000	2.417886000
1	-5.446647000	2.669697000	2.786124000
1	5.503033000	2.949037000	2.525071000
7	4.046281000	0.318255000	1.306625000
7	-3.888934000	0.169193000	1.431620000
7	-1.369962000	-1.164172000	0.039875000
6	-0.573805000	-1.843720000	0.877476000
6	-0.782753000	-0.319039000	-0.832109000
6	0.808021000	-1.738832000	0.805717000
1	-1.020801000	-2.509394000	1.603402000
6	0.600573000	-0.228506000	-0.915085000
6	-1.693820000	0.506175000	-1.732939000
7	1.398824000	-0.961253000	-0.124140000
6	1.709925000	-2.506703000	1.761769000
1	1.049573000	0.427738000	-1.647021000
8	-1.187329000	1.278031000	-2.527863000
8	-2.950036000	0.289820000	-1.526496000
8	1.199011000	-3.110285000	2.686711000
8	2.966798000	-2.394098000	1.484985000

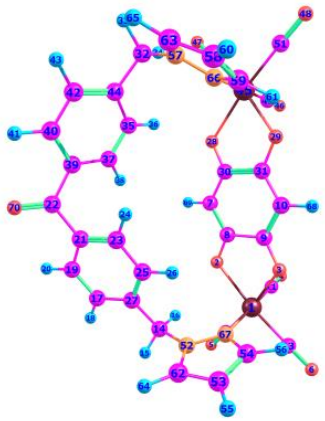
Cartesian coordinates of the optimized structure of 3 (Helicate)



Atom	X	Y	Z
75	-4.341940000	-0.944405000	0.521146000
75	3.748583000	-1.210362000	-0.776484000
8	-2.470096000	0.098752000	0.955786000
8	1.996123000	-2.532067000	-0.447102000
8	-2.705707000	-2.279599000	-0.110955000
8	2.067736000	0.071475000	-0.205171000
8	-6.642398000	-2.693506000	-0.554571000
7	-4.014444000	0.016339000	-1.523208000
7	4.421375000	-0.316901000	2.371027000
8	5.935779000	0.869167000	-1.380289000
7	3.971589000	-1.249539000	1.484047000
7	-3.929759000	1.328200000	-1.890668000
8	3.107594000	-1.230477000	-3.799869000
8	5.797406000	-3.484170000	-1.151054000
6	-1.386011000	-0.448780000	0.577337000
6	0.954995000	-0.480667000	0.056136000
6	0.875047000	-1.970594000	-0.231355000
6	-5.805076000	-2.022739000	-0.131122000
6	-0.367991000	-2.601438000	-0.281661000
1	-0.448578000	-3.638603000	-0.583884000
6	2.176987000	4.020550000	0.749409000
8	-4.511118000	-2.358381000	3.262987000
6	-1.514873000	-1.861186000	0.023179000
8	-6.355769000	1.158422000	1.531209000
6	-0.147966000	0.183597000	0.590041000
1	-0.073995000	1.215944000	0.892467000
6	4.993734000	0.980460000	1.996898000
1	5.720772000	0.815790000	1.204050000
1	5.562952000	1.302206000	2.873285000
6	3.996488000	2.054342000	1.595914000
6	-2.597170000	3.177631000	-0.826088000
6	-0.183121000	3.207379000	-0.905044000
1	0.743116000	2.711071000	-1.172022000
6	-0.151708000	4.412106000	-0.198369000
6	3.496008000	4.036508000	0.289720000

1	3.805012000	4.796891000	-0.419299000
6	5.121791000	0.083083000	-1.131391000
6	-1.394359000	2.609040000	-1.236687000
1	-1.387870000	1.664228000	-1.766023000
6	5.052792000	-2.612246000	-1.030539000
6	-5.615699000	0.359869000	1.140856000
6	1.802497000	3.056684000	1.691371000
1	0.790606000	3.051133000	2.082141000
6	-4.454731000	-1.833463000	2.240906000
6	3.352585000	-1.227570000	-2.675831000
6	-3.920006000	2.439751000	-0.939420000
1	-4.168634000	2.017642000	0.031768000
1	-4.729137000	3.123422000	-1.209688000
6	-2.570170000	4.420448000	-0.178275000
1	-3.500557000	4.891165000	0.127206000
6	-1.361885000	5.043591000	0.113223000
1	-1.344757000	6.002182000	0.620439000
6	4.304622000	-0.780601000	3.638461000
1	4.620489000	-0.176414000	4.474501000
6	3.573952000	-2.292884000	2.221565000
1	3.169208000	-3.162778000	1.728796000
6	4.388233000	3.046229000	0.691025000
1	5.387212000	3.028621000	0.267979000
6	2.708523000	2.098332000	2.128013000
1	2.385682000	1.350465000	2.844547000
6	3.761723000	-2.047198000	3.586289000
1	3.538544000	-2.701781000	4.412859000
6	1.163729000	5.004978000	0.226028000
6	-3.952142000	-0.683822000	-2.661038000
1	-3.996044000	-1.760925000	-2.623871000
6	-3.831959000	0.163659000	-3.768965000
1	-3.763443000	-0.113093000	-4.808368000
6	-3.821951000	1.435756000	-3.235066000
1	-3.732038000	2.404481000	-3.701524000
8	1.393028000	6.194678000	0.153219000

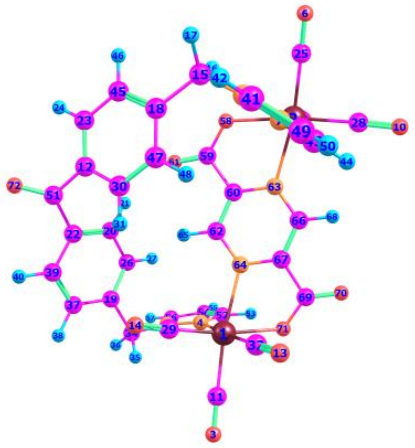
Cartesian coordinates of the optimized structure of 3 (Mesocate)



Atom	X	Y	Z
75	-4.279898000	-1.289453000	-0.176037000
8	-2.493419000	-0.331440000	-1.032170000
8	-2.553583000	-1.924191000	1.033803000
8	-4.037764000	-3.717150000	-2.074874000
8	-6.422437000	-0.087748000	-2.037228000
8	-6.446978000	-2.769913000	1.439841000
6	-0.137485000	-0.320965000	-1.155319000
6	-1.357080000	-0.699741000	-0.596576000
6	-1.392712000	-1.618228000	0.620558000
6	-0.204064000	-2.064577000	1.202111000
6	-4.128931000	-2.814398000	-1.368570000
6	-5.635919000	-0.553198000	-1.329436000
6	-5.657797000	-2.209124000	0.812309000
6	-4.311729000	2.396325000	-0.228961000
1	-5.203356000	2.986002000	-0.453600000
1	-4.260945000	1.588879000	-0.957812000
6	-3.018492000	4.378510000	-1.127999000
1	-3.916425000	4.704289000	-1.645266000
6	-1.835214000	5.092471000	-1.292392000
1	-1.804724000	5.977709000	-1.917864000
6	-0.659607000	4.662959000	-0.668061000
6	0.628679000	5.405849000	-0.880438000
6	-0.713158000	3.547451000	0.177117000
1	0.177243000	3.216955000	0.696832000
6	-1.897846000	2.850496000	0.357373000
1	-1.911424000	1.985367000	1.009646000
6	-3.055902000	3.239834000	-0.316167000
8	2.205039000	-0.589995000	-1.081477000
8	2.149330000	-2.121046000	1.024504000
6	1.046446000	-0.825187000	-0.615884000
6	1.012209000	-1.724512000	0.613066000
6	5.190580000	1.960422000	0.074299000
1	6.128884000	2.475626000	0.287134000
1	5.388991000	1.231699000	-0.705653000
6	3.043348000	2.485900000	-1.122697000

1	3.045478000	1.480346000	-1.524557000
6	1.937121000	3.298433000	-1.328956000
1	1.099774000	2.919555000	-1.903252000
6	1.882282000	4.583874000	-0.779552000
6	2.994359000	5.075460000	-0.089409000
1	2.973839000	6.090050000	0.293283000
6	4.087695000	4.247304000	0.147442000
1	4.925854000	4.624490000	0.727095000
6	4.102267000	2.932170000	-0.330793000
75	3.919334000	-1.661327000	-0.207409000
8	3.429444000	-4.119481000	-2.011309000
8	6.094407000	-0.759532000	-2.191837000
8	5.985699000	-3.266716000	1.422681000
6	3.612161000	-3.200607000	-1.344609000
6	5.296806000	-1.103867000	-1.427148000
6	5.233691000	-2.662642000	0.791027000
7	-4.490241000	1.770223000	1.082466000
6	-4.642823000	1.490455000	3.270237000
6	-4.421749000	0.268222000	2.624090000
1	-4.766176000	1.666464000	4.326441000
1	-4.332272000	-0.722476000	3.040980000
7	4.835447000	1.222693000	1.299969000
6	4.295036000	0.858645000	3.415083000
6	3.813676000	-0.165248000	2.592185000
1	4.202864000	0.944719000	4.485550000
1	3.270713000	-1.059906000	2.852303000
6	-4.675308000	2.422425000	2.253205000
6	4.932453000	1.725320000	2.552500000
1	-4.793478000	3.494565000	2.271360000
1	5.435586000	2.662551000	2.730512000
7	4.133446000	0.053787000	1.309697000
7	-4.329382000	0.435503000	1.300208000
1	-0.231337000	-2.723214000	2.061794000
1	-0.114725000	0.309900000	-2.035389000
8	0.653396000	6.601970000	-1.095098000

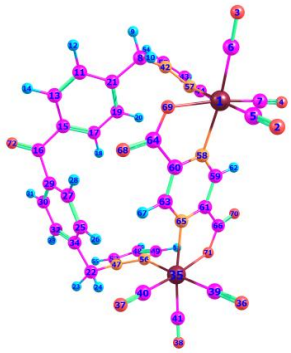
Cartesian coordinates of the optimized structure of 4 (Helicate)



Atom	X	Y	Z
75	-3.106242000	-1.368002000	0.761576000
75	3.876882000	-0.813206000	-0.605205000
8	-5.938542000	-2.160133000	1.728328000
7	-3.879209000	-1.096633000	-1.371772000
7	3.652195000	1.310718000	2.001542000
8	6.789087000	0.237564000	-0.596456000
7	3.493908000	0.048503000	1.503767000
7	-4.641932000	-0.119971000	-1.949692000
8	4.267915000	-1.940426000	-3.454293000
8	4.777601000	-3.509867000	0.598040000
6	-4.885995000	-1.852913000	1.382296000
6	0.052526000	4.564194000	0.315199000
8	-1.957732000	-2.048286000	3.547588000
8	-3.396043000	1.473495000	1.917087000
6	3.763975000	2.516302000	1.178009000
1	4.144075000	2.215844000	0.203455000
1	4.518313000	3.152546000	1.648206000
6	2.455162000	3.268980000	0.989998000
6	-4.179275000	2.223824000	-1.148187000
6	-1.961852000	3.152814000	-1.400676000
1	-0.950297000	3.050037000	-1.776218000
6	-2.302417000	4.226763000	-0.573743000
6	1.283234000	5.119585000	-0.050249000
1	1.299490000	6.039877000	-0.623594000
6	5.713121000	-0.169487000	-0.597010000
6	-2.903940000	2.173755000	-1.705878000
1	-2.616652000	1.342206000	-2.340206000
6	4.467776000	-2.495536000	0.139047000
6	-3.343072000	0.426476000	1.425305000
6	0.043173000	3.401404000	1.089681000
1	-0.900432000	2.978298000	1.417481000
6	-2.387736000	-1.793733000	2.511317000
6	4.125020000	-1.524197000	-2.392050000
6	-5.148606000	1.058145000	-1.248646000
1	-5.452308000	0.738798000	-0.250595000

1	-6.061760000	1.351753000	-1.772137000
6	-4.545876000	3.347998000	-0.399453000
1	-5.543409000	3.414198000	0.026169000
6	-3.624141000	4.354514000	-0.134491000
1	-3.904398000	5.210713000	0.469473000
6	3.539672000	1.305783000	3.349192000
1	3.616514000	2.226291000	3.906780000
6	3.289927000	-0.732966000	2.573295000
1	3.164147000	-1.796326000	2.446300000
6	2.468135000	4.466069000	0.264753000
1	3.411102000	4.872989000	-0.089252000
6	1.233323000	2.772761000	1.443143000
1	1.194119000	1.870635000	2.043652000
6	3.307981000	0.008900000	3.758304000
1	3.180088000	-0.351985000	4.765718000
6	-1.239623000	5.195297000	-0.129073000
6	-3.662184000	-2.001963000	-2.334284000
1	-3.115181000	-2.899020000	-2.093233000
6	-4.263046000	-1.614594000	-3.537043000
1	-4.260749000	-2.144042000	-4.475748000
6	-4.876076000	-0.413648000	-3.250073000
1	-5.461470000	0.252388000	-3.864615000
8	2.974046000	1.018739000	-1.332022000
6	1.691522000	1.110215000	-1.393034000
6	0.962106000	-0.083995000	-0.794080000
8	1.028412000	1.999770000	-1.898384000
6	-0.390791000	-0.045080000	-0.483646000
7	1.678338000	-1.209091000	-0.599202000
7	-1.044120000	-1.145397000	-0.093498000
1	-0.936607000	0.885163000	-0.534282000
6	0.998000000	-2.338191000	-0.334791000
6	-0.376095000	-2.317199000	-0.133923000
1	1.539130000	-3.273373000	-0.272715000
6	-1.214007000	-3.590223000	-0.021245000
8	-0.651994000	-4.664080000	-0.109355000
8	-2.482288000	-3.351565000	0.078171000
8	-1.412395000	6.396835000	-0.122241000

Cartesian coordinates of the optimized structure of 4 (Mesocate)



Atom	X	Y	Z
75	-3.638119000	-1.380683000	-0.294350000
8	-3.137581000	-3.406988000	-2.572726000
8	-6.621433000	-1.227473000	-1.104250000
8	-4.216499000	-3.714636000	1.640905000
6	-3.320911000	-2.654733000	-1.722914000
6	-5.516015000	-1.300255000	-0.794468000
6	-4.027349000	-2.841593000	0.907586000
6	-4.621034000	2.195955000	0.150386000
1	-5.568173000	2.740004000	0.155210000
1	-4.614433000	1.538526000	-0.717986000
6	-3.487172000	4.254693000	-0.777149000
1	-4.398261000	4.479675000	-1.324120000
6	-2.368272000	5.062431000	-0.949722000
1	-2.403835000	5.921633000	-1.610332000
6	-1.167930000	4.747496000	-0.305586000
6	0.076965000	5.546449000	-0.549767000
6	-1.137856000	3.662691000	0.575784000
1	-0.224612000	3.423719000	1.107925000
6	-2.265356000	2.880677000	0.775640000
1	-2.213134000	2.043900000	1.461945000
6	-3.439128000	3.142888000	0.069891000
6	4.797519000	2.184089000	-0.118742000
1	5.742137000	2.725928000	-0.043088000
1	4.899446000	1.473808000	-0.933054000
6	2.556285000	2.738360000	-1.133202000
1	2.607768000	1.807859000	-1.683154000
6	1.409160000	3.517935000	-1.210567000
1	0.556491000	3.157819000	-1.776680000
6	1.352172000	4.747516000	-0.545189000
6	2.478644000	5.206414000	0.143353000
1	2.450804000	6.183188000	0.614211000
6	3.602618000	4.394076000	0.261406000
1	4.452677000	4.743684000	0.840547000
6	3.639445000	3.134715000	-0.347894000
75	3.568014000	-1.477698000	-0.262164000
8	3.008478000	-3.995266000	-1.960895000
8	4.114449000	0.005355000	-2.908178000
8	6.545059000	-2.299009000	-0.038064000
6	3.212004000	-3.053267000	-1.334765000

6	3.937911000	-0.534851000	-1.897386000
6	5.443541000	-1.988512000	-0.136167000
7	-4.598360000	1.359794000	1.351835000
6	-4.565198000	0.799032000	3.491581000
6	-4.015995000	-0.214170000	2.699422000
1	-4.696764000	0.802531000	4.561284000
1	-3.641176000	-1.178239000	3.003569000
7	4.669429000	1.420309000	1.134375000
6	4.631349000	0.979817000	3.302683000
6	4.031071000	-0.051300000	2.574240000
1	4.776566000	1.034387000	4.369273000
1	3.635542000	-0.993775000	2.915526000
6	-4.917394000	1.786097000	2.594838000
6	5.020880000	1.896530000	2.350676000
1	-5.352569000	2.762117000	2.743192000
1	5.519036000	2.848598000	2.443281000
7	4.040105000	0.212362000	1.258823000
7	-4.025732000	0.122443000	1.402075000
7	-1.426748000	-1.224706000	0.052147000
6	-0.644396000	-1.921385000	0.889955000
6	-0.815213000	-0.400887000	-0.824433000
6	0.741525000	-1.848869000	0.818484000
1	-1.105801000	-2.570473000	1.622055000
6	0.568119000	-0.367618000	-0.926419000
6	-1.697126000	0.491452000	-1.688490000
7	1.352072000	-1.105339000	-0.126511000
6	1.628479000	-2.605193000	1.798281000
1	1.027650000	0.250586000	-1.682694000
8	-1.162321000	1.310896000	-2.415823000
8	-2.958615000	0.286770000	-1.515056000
8	1.102469000	-3.191230000	2.725859000
8	2.889228000	-2.495173000	1.538835000
8	0.062412000	6.747878000	-0.726304000

Table S1. Total Energy and difference in energies of complexes 1–4 (helicates and mesocates).

Complexes	Helicate	Mesocate	Energy Difference	
	Total Energy(Hartree)		Hartree	kcal/mol
1	−2399.502304	−2399.503030	0.000726	0.456
2	−2509.055163	−2509.061627	0.006464	4.056
3	−2473.529280	−2473.537279	0.007999	5.019
4	−2583.086966	−2583.093025	0.006059	3.802

Table S2. Crystal data and structure refinement for 1.

Empirical formula	$C_{93}H_{80}N_8O_{20}Re_4$
Formula weight	2374.45
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P−1
Unit cell dimensions	*a* = 8.9621(4) Å α = 83.058(3)°.
	b = 10.8991(3) Å β = 86.516(3)°.
	c = 23.4881(7) Å γ = 79.937(3)°.
Volume	2240.59(14) Å^3
Z	1
Density (calculated)	1.760 mg/m^3
Absorption coefficient	5.460 mm^{-1}
F(000)	1154
Crystal size	0.160 x 0.140 x 0.120 mm^3
Theta range for data collection	1.910 to 25.000°.
Index ranges	−10 <= h <= 10, −12<=k<=12, −26<=l<=27
Reflections collected	33548
Independent reflections	7882 [$R_{(int)}$ = 0.0792]
Completeness to theta = 25.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.560 and 0.475
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7882 / 642 / 695
Goodness-of-fit on F^2	1.007
Final R indices [I>2σ(I)]	R_1= 0.0459, wR_2= 0.1137
R indices (all data)	R_1= 0.0670, wR_2= 0.1289
Extinction coefficient	n/a
Largest diff. peak and hole	1.939 and −1.111 e.Å^{-3}

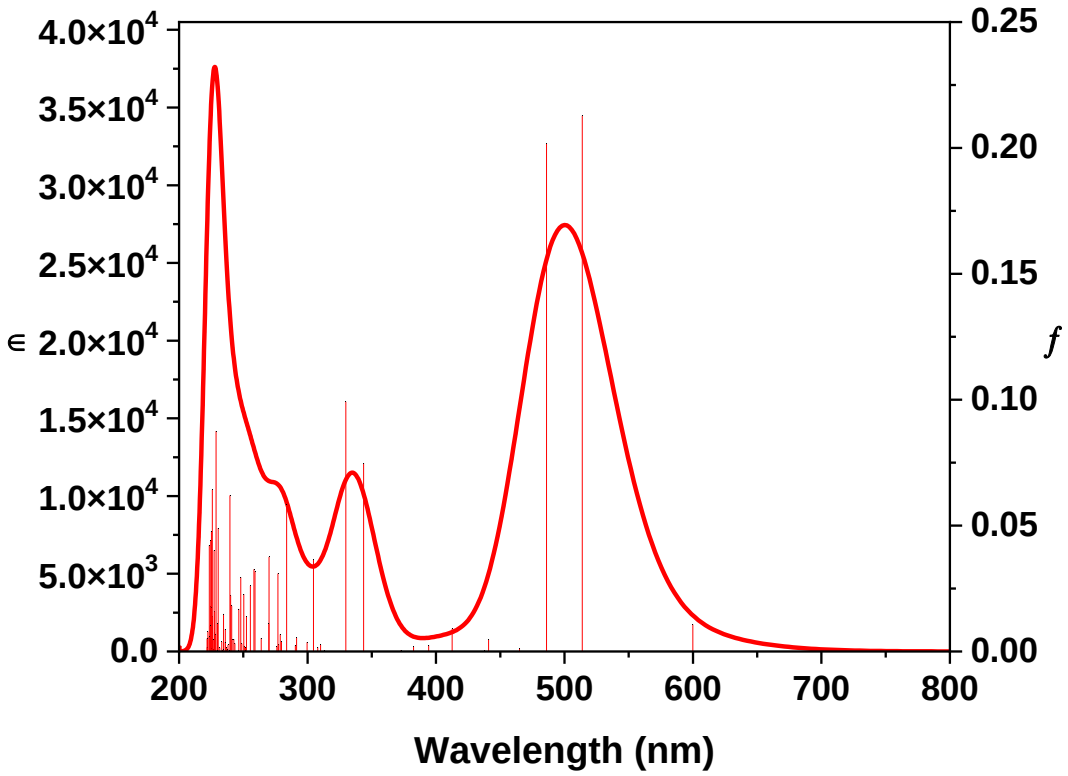


Figure S26. Simulated absorption spectrum of **1** in DMSO with oscillator strength (ƒ) values (shown as vertical bars, same color code).

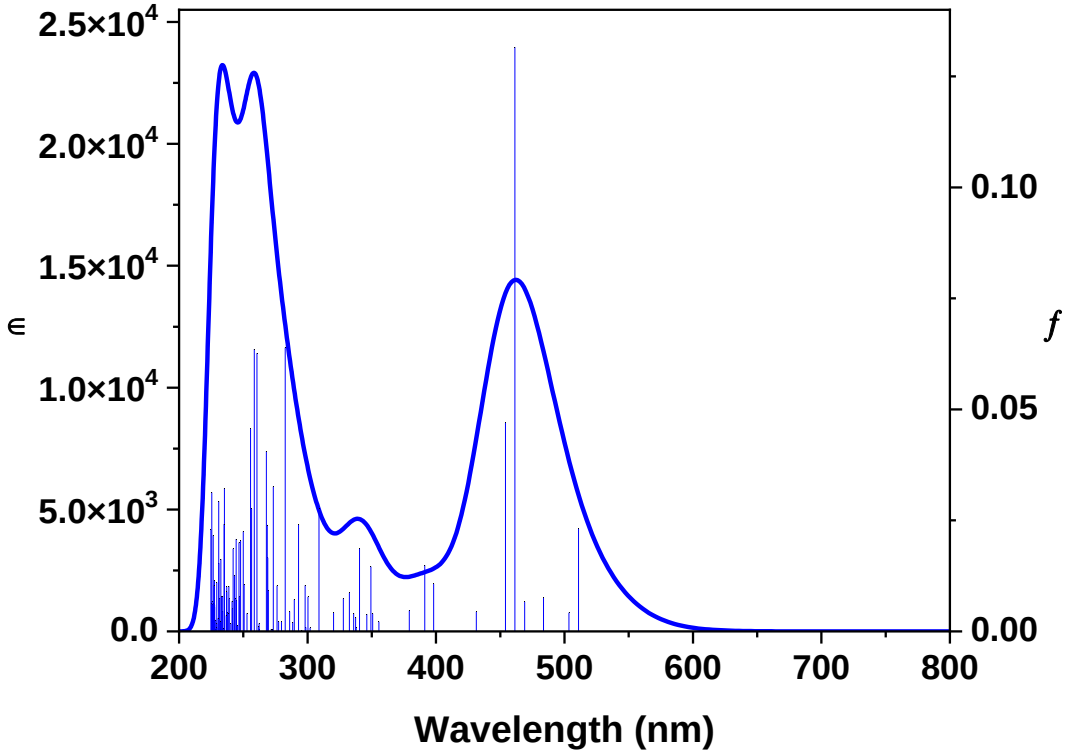


Figure S27. Simulated absorption spectrum of **2** in DMSO with oscillator strength (*f*) values (shown as vertical bars, same color code).

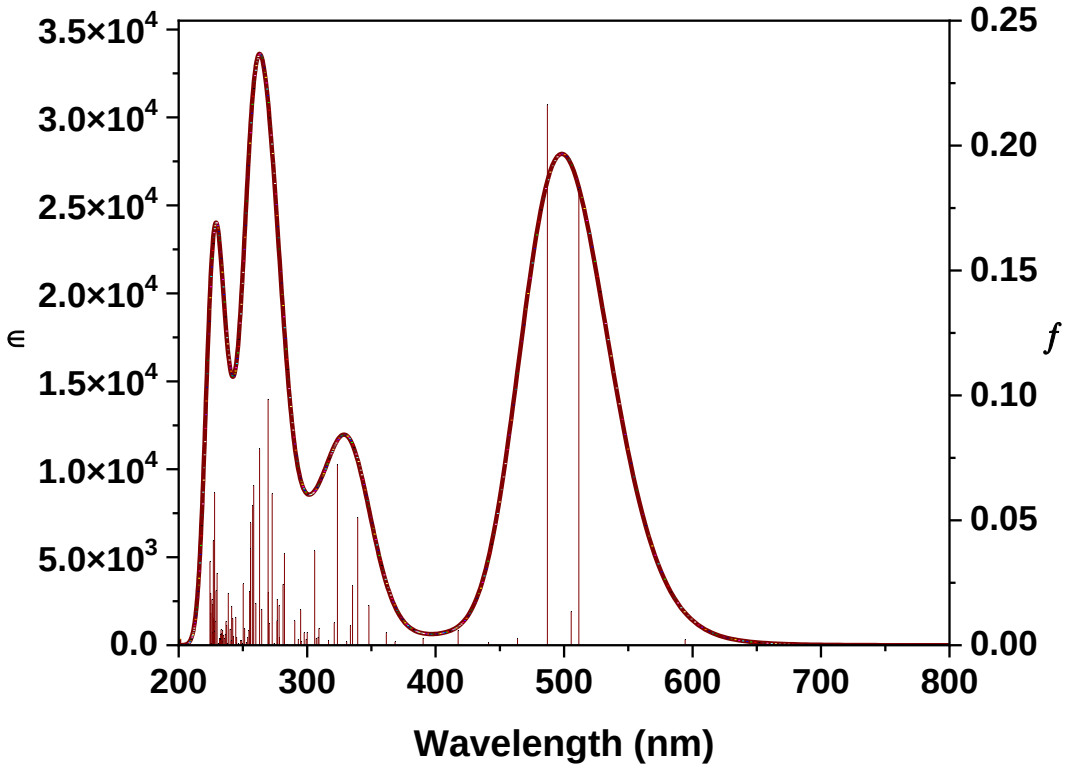


Figure S28. Simulated absorption spectrum of **3** in DMSO with oscillator strength (ƒ) values (shown as vertical bars, same color code).

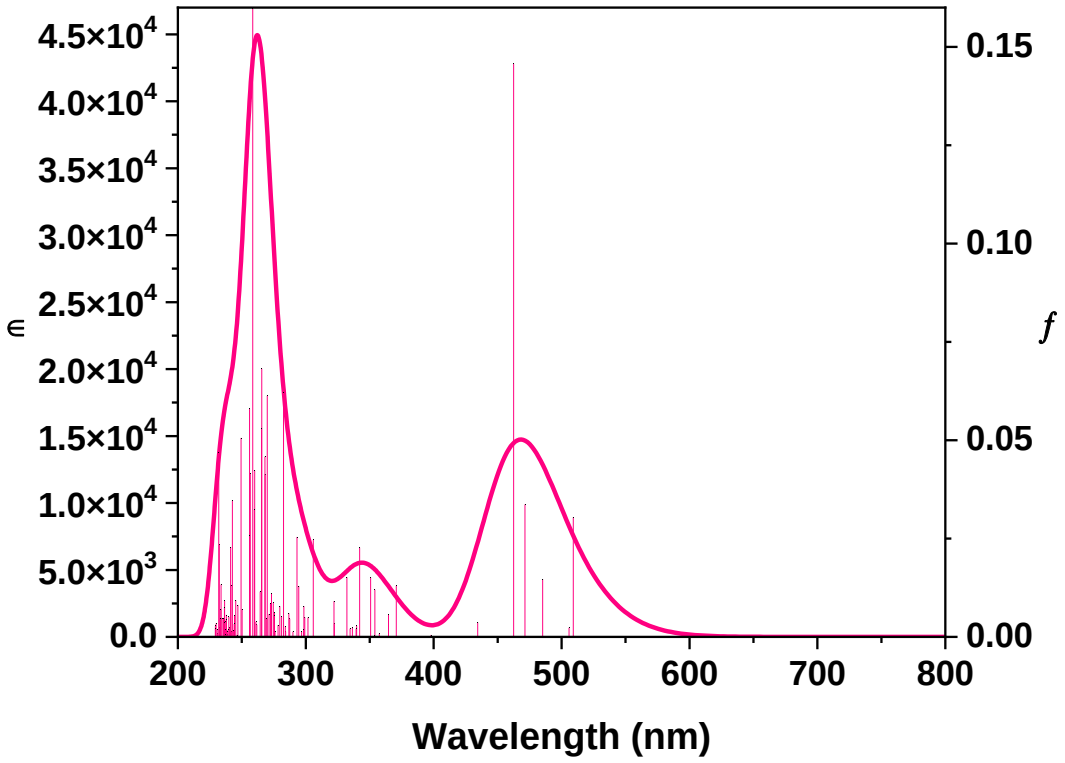


Figure S29. Simulated absorption spectrum of **4** in DMSO with oscillator strength (ƒ) values (shown as vertical bars, same color code).

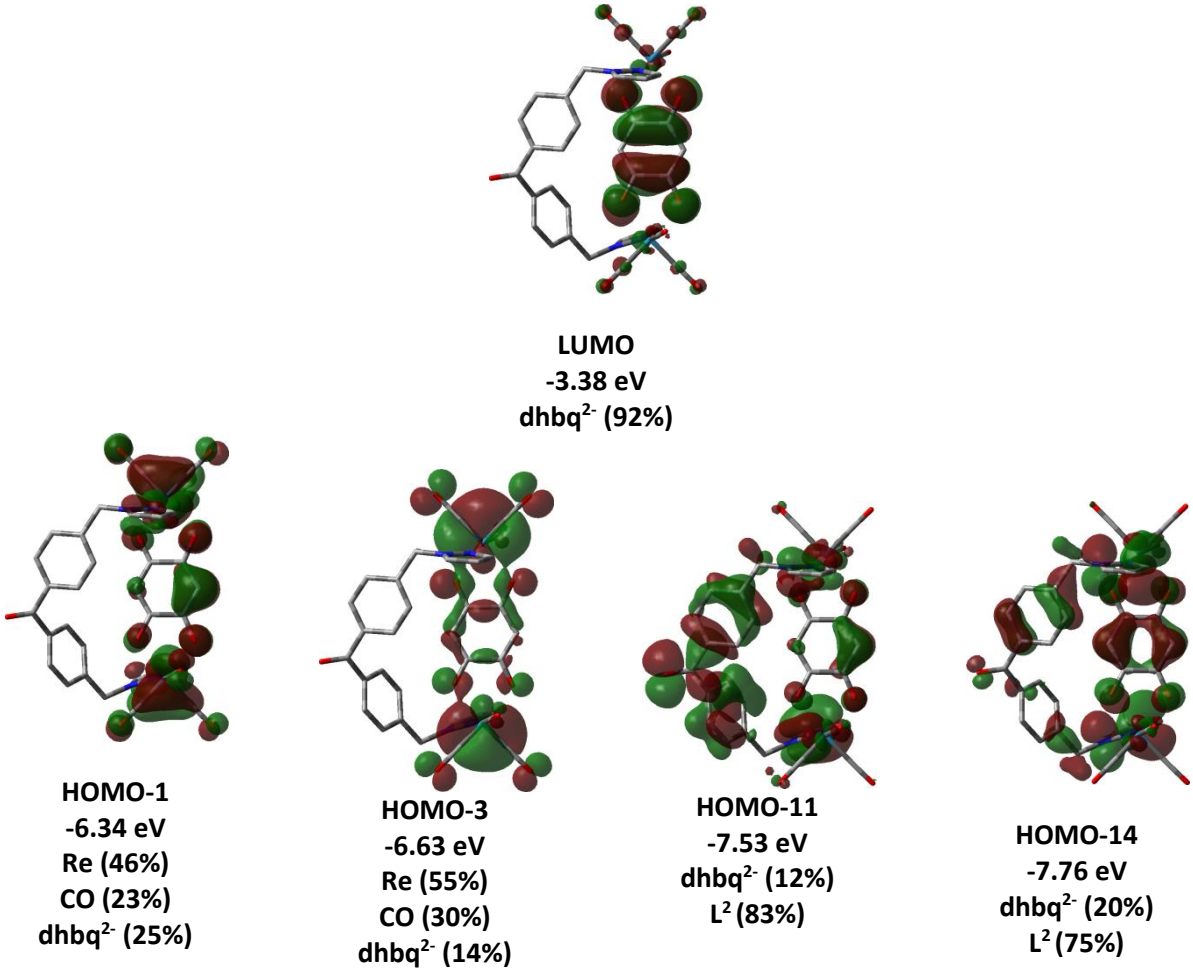
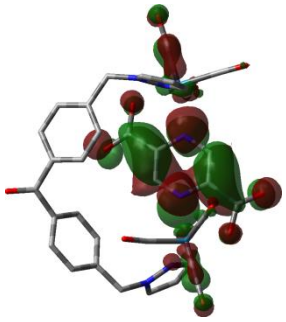
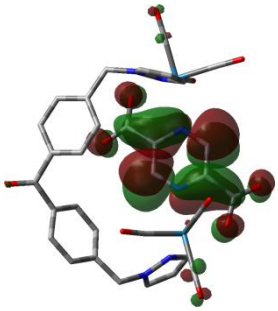


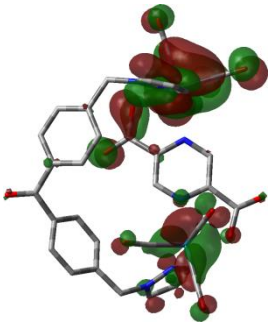
Figure S30. Frontier molecular orbitals involved in TDDFT/IEF-PCM transitions of **3**.



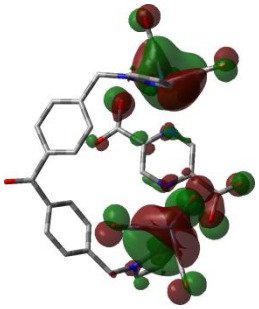
LUMO
-3.42 eV
pydc^{2-} (91%)



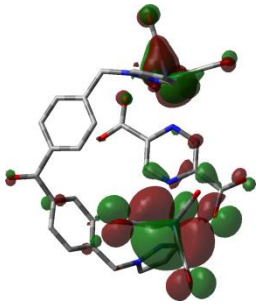
LUMO+1
-2.37 eV
pydc^{2-} (95%)



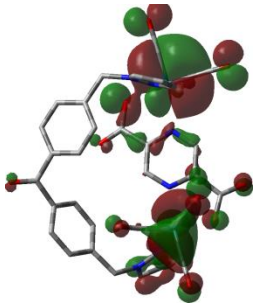
HOMO
-6.55 eV
Re (55%)
CO (25%)
pydc^{2-} (10%)



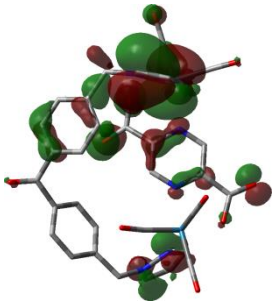
HOMO-2
-6.7 eV
Re (59%)
CO (27%)
pydc^{2-} (10%)



HOMO-3
-6.76 eV
Re (60%)
CO (28%)
pydc^{2-} (8%)



HOMO-4
-6.81 eV
Re (58%)
CO (27%)
pydc^{2-} (9%)



HOMO-15
-8.1 eV
pydc^{2-} (14%)
L^{2} (78%)

Figure S31. Frontier molecular orbitals involved in TDDFT/IEF-PCM transitions of **4**.

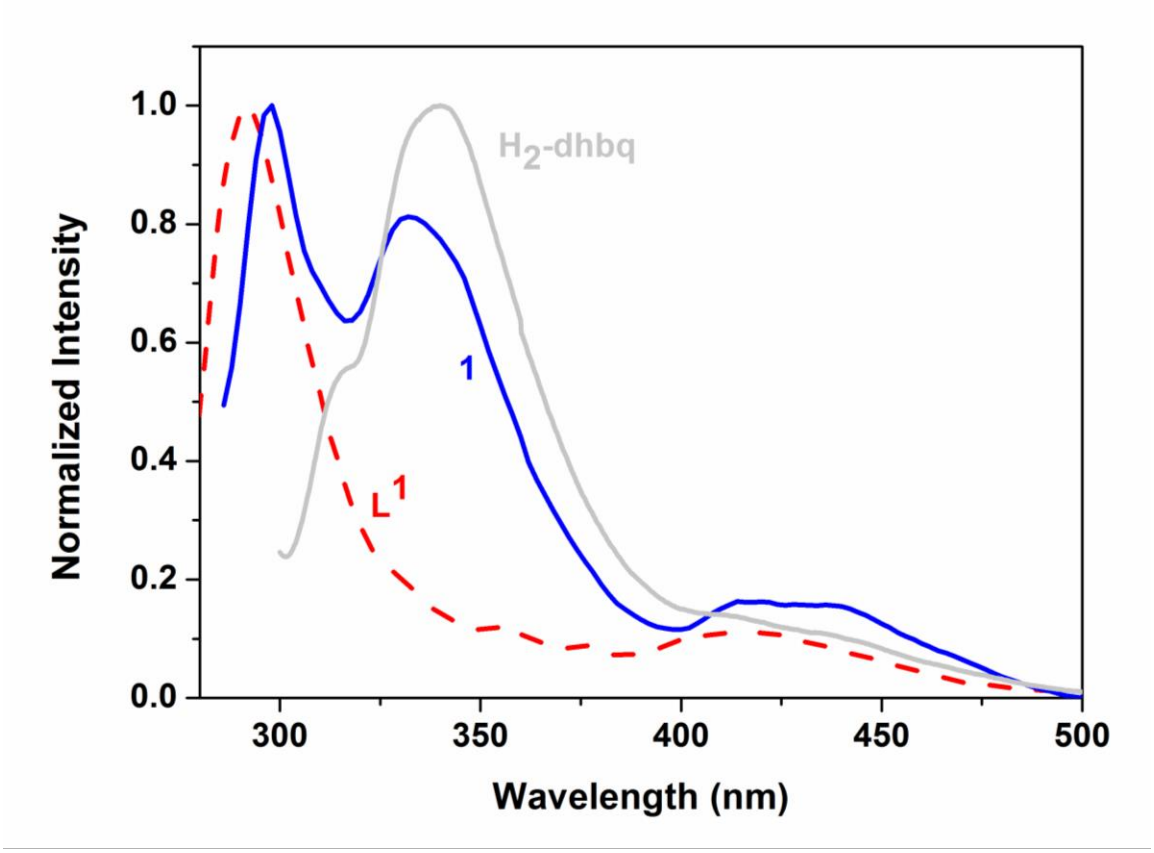


Figure S32. Emission spectra of **1** (λ_{exc} = 270 nm), L^1 (λ_{exc} = 265 nm), and H_2-dhbq (λ_{exc} = 285 nm) in DMSO.

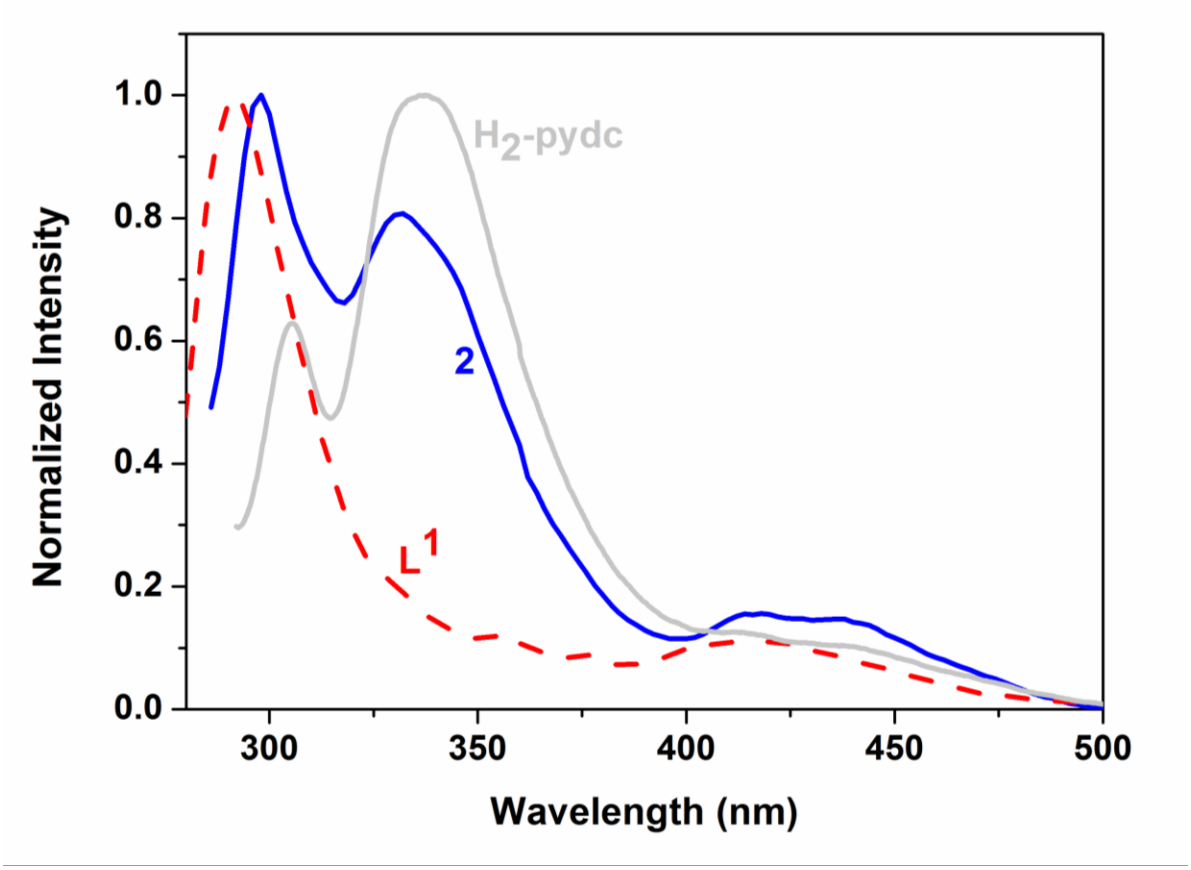


Figure S33. Emission spectra of **2** (λ_{exc} = 270 nm), L^1 (λ_{exc} = 265 nm), and H_2-pydc (λ_{exc} = 277 nm) in DMSO.

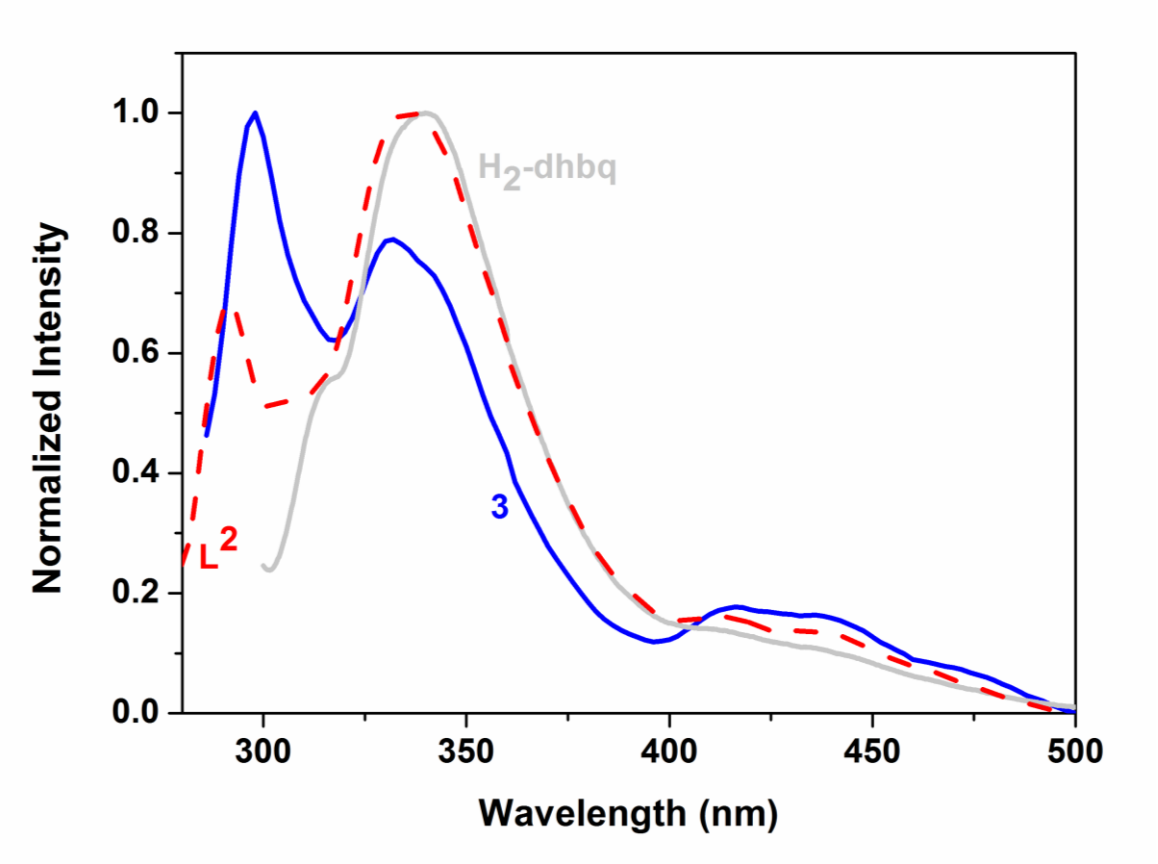


Figure S34. Emission spectra of **3** (λ_{exc} = 270 nm), L^2 (λ_{exc} = 265 nm), and H_2-dhbq (λ_{exc} = 285 nm) in DMSO.

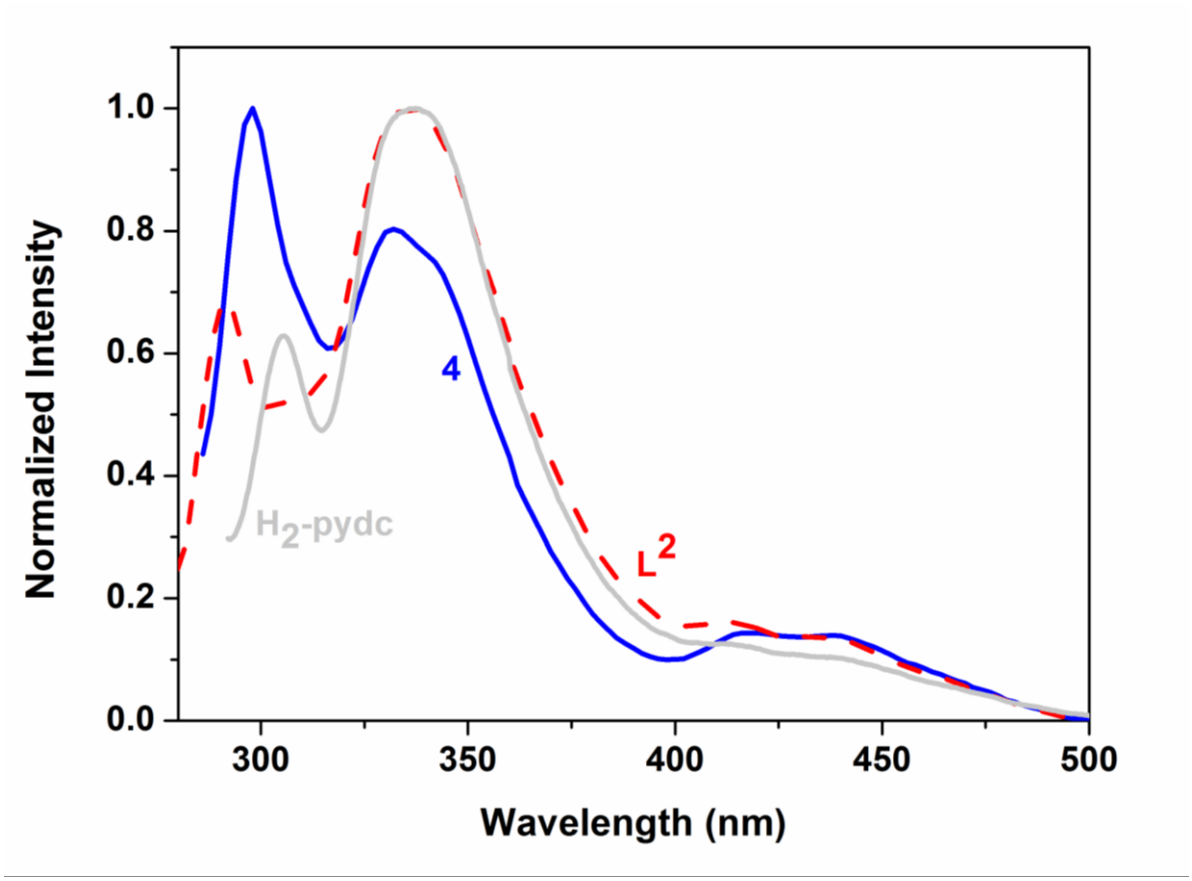


Figure S35. Emission spectra of **4** (λ_{exc} = 270 nm), L^2 (λ_{exc} = 265nm), and H_2-pydc (λ_{exc} = 277 nm) in DMSO.

Table S3. Major singlet excited state transitions for 3 from TDDFT/IEF-PCM calculations with DMSO as the solvent model.

Trans band	Wavelength (nm)	Oscillator strength (f)	Major contribution [%]	Character
2	512	0.1824	H-3 → LUMO (30%), H-1 → LUMO (61%)	Re (46%) CO (23 %) dhbq^{2-} (25%) → dhbq^{2-} (92%)
4	487	0.2164	H-3 → LUMO (65%), H-1 → LUMO (32%)	Re (55%) CO (30 %) dhbq^{2-} (14 %) → dhbq^{2-} (92%)
12	339	0.0512	H-11 → LUMO (84%)	dhbq^{2-} (12 %) L^{2} (83%) → dhbq^{2-} 92%)
16	324	0.0725	H-14 → LUMO (76%)	dhbq^{2-} (20 %) L^{2} (75%) → dhbq^{2-} 92%)

Table S4. Major singlet excited state transitions for 4 from TDDFT/IEF-PCM calculations with DMSO as the solvent model.

Trans band	Wavelength (nm)	Oscillator strength (f)	Major contribution [%]	Character
1	509	0.0304	HOMO → LUMO (90%)	Re (55%) CO (25%) pydc^{2-} 10%) → pydc^{2-} (91%)
5	463	0.1457	H-4 → LUMO (39%), H-3 → LUMO (29%), H-2 → LUMO (20%)	Re (58%) CO (27%) pydc^{2-} (9%) → pydc^{2-} (91%)
14	342	0.0227	H-2 → L+1 (92%)	Re (59%) CO (27%) pydc^{2-} (10%) → pydc^{2-} (95%)
23	306	0.0247	H-15 → LUMO (96%)	pydc^{2-} (14 %) L^{2} (78%) → pydc^{2-} (91%)

Table S5. Free energies of activation calculated from the coalescence temperatures and the chemical shifts (^{1}H NMR, 500 MHz) of the signals of dhbq^{2-} protons in 1 and 3, pydc^{2-} protons in 2 and 4.

	δ (ppm)	δ (ppm)	Δδ (ppm)	Δν (Hz)	Tc (K)	ΔG‡ (J/mol)	ΔG‡ (Kcal/mol)
1	5.787	5.785	0.002	1	373	89565	21.4
3	5.788	5.786	0.002	1	373	89565	21.4
2	9.144	9.124	0.02	10	358	78988	18.8
4	9.144	9.124	0.02	10	358	78988	18.8

$$\Delta G^{\ddagger} = \mathrm{RT_c}\left[22.96 + \ln\left(\frac{\mathrm{T_c}}{\Delta \nu}\right)\right]$$

Where:

R is the gas constant.

$\Delta\nu$ is the chemical shift difference (Hz) between the two exchanging nuclei at temperature below coalescence.

Tc is the coalescence temperature.

$\Delta G^{\ddagger}$ is the free energy of activation.