Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Reductive O-Triflylation of Naphthalene Diimide: Access to Alkyne- and Amine-functionalized 2,7-Diazapyrenes

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Density functional theory (DFT)

Kohn-Sham frontier molecular orbitals and optimized geometries

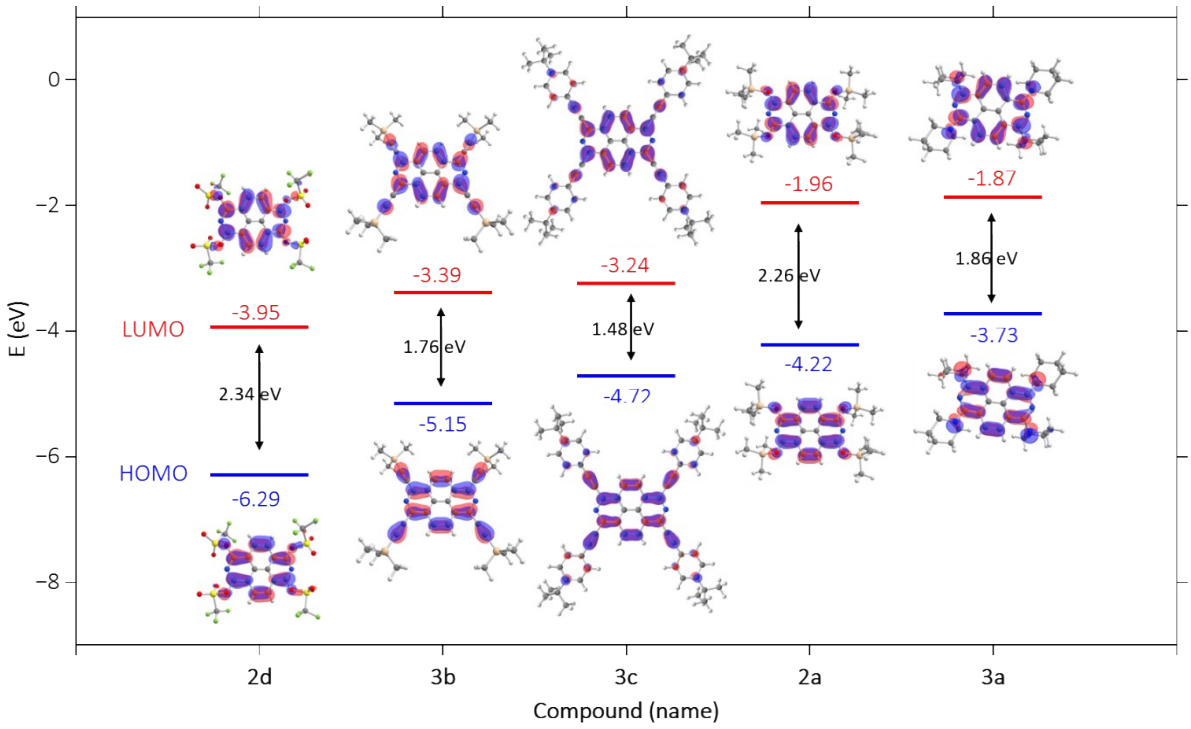


Figure S1. Kohn-Sham orbitals of HOMO and LUMO of **2a**, **2d**, **3a**, **3b** and **3c**, and their energies calculated by DFT (def2-TZVPP/PBE level of theory).

Table S1. Cartesian coordinates (XYZ) of DFT optimized geometry of **2d** (def2-TZVPP/PBE).

C	-2.759505000	1.260306000	0.603317000
C	-1.391672000	1.372323000	0.286771000
C	-0.698449000	0.137576000	0.124201000
C	-1.376063000	-1.106231000	0.275932000
C	-2.738411000	-1.012287000	0.620135000
N	-3.399768000	0.119167000	0.786372000
C	-0.683868000	2.605966000	0.136278000
C	0.650423000	2.613908000	-0.163585000
C	1.366657000	1.388846000	-0.341810000
C	0.681902000	0.146029000	-0.207203000
C	1.367983000	-1.089357000	-0.386981000
C	0.665179000	-2.324298000	-0.229518000
C	-0.664816000	-2.332461000	0.090682000
C	2.735180000	1.293376000	-0.660791000
N	3.383206000	0.161072000	-0.869599000
C	2.729619000	-0.978342000	-0.728953000
O	-3.470644000	2.434788000	0.835115000
S	-4.828543000	2.801207000	-0.031497000
O	-5.680020000	3.515782000	0.874340000
O	-5.239999000	1.695077000	-0.849845000
C	-4.046896000	4.075545000	-1.181327000
F	-3.466544000	5.052868000	-0.469745000
F	-5.010107000	4.591488000	-1.951518000
F	-3.122907000	3.480631000	-1.953650000
O	-3.420179000	-2.194536000	0.863175000
S	-4.921959000	-2.406175000	0.187370000
O	-4.978770000	-1.748873000	-1.090624000
O	-5.924401000	-2.280865000	1.206533000
C	-4.651980000	-4.249184000	-0.118454000

F	-5.773054000	-4.734687000	-0.664138000
F	-4.397634000	-4.881402000	1.032751000
F	-3.626240000	-4.429019000	-0.964656000
O	3.419295000	-2.150155000	-0.998550000
S	4.923327000	-2.366179000	-0.329033000
O	4.976657000	-1.737639000	0.963496000
O	5.923864000	-2.210584000	-1.345894000
C	4.666704000	-4.217530000	-0.064916000
F	4.415484000	-4.825240000	-1.229921000
F	5.791823000	-4.707339000	0.468462000
F	3.643258000	-4.423760000	0.778026000
O	3.438204000	2.477681000	-0.866106000
S	4.793877000	2.833913000	0.008137000
O	5.638261000	3.577597000	-0.880750000
O	5.215478000	1.711427000	0.798550000
C	4.003350000	4.073080000	1.189915000
F	3.085472000	3.451725000	1.948600000
F	4.963364000	4.578001000	1.971315000
F	3.413852000	5.062699000	0.503265000
H	-1.222325000	3.541710000	0.272969000
H	1.182462000	3.556146000	-0.279127000
H	1.206830000	-3.257846000	-0.370696000
H	-1.200053000	-3.272645000	0.210681000

Table S2. Cartesian coordinates (XYZ) of DFT optimized geometry of **3b** (def2-TZVPP/PBE).

C	-3.160475000	1.164221000	-0.212204000
C	-1.738544000	1.238113000	-0.110055000
C	-1.027614000	0.009050000	-0.070901000
C	-1.730261000	-1.223809000	-0.133226000
C	-3.152651000	-1.157580000	-0.234415000
N	-3.835746000	0.001496000	-0.271987000
C	-1.010738000	2.463097000	-0.046467000
C	0.357516000	2.466813000	0.051831000
C	1.093473000	1.245763000	0.093541000
C	0.390882000	0.012864000	0.031158000
C	1.101821000	-1.216200000	0.070516000
C	0.374044000	-2.441145000	0.006107000
C	-0.994210000	-2.444827000	-0.092264000
C	2.515741000	1.179560000	0.195948000
N	3.198844000	0.020509000	0.233945000
C	2.523714000	-1.142236000	0.173612000
C	-3.928510000	2.361928000	-0.254680000
C	-3.912581000	-2.359400000	-0.300198000
C	3.292077000	-2.339740000	0.215978000
C	3.275777000	2.381277000	0.262106000
C	-4.551129000	3.417099000	-0.287962000
C	3.891635000	3.439534000	0.316601000
C	3.914228000	-3.395183000	0.249595000
C	-4.528099000	-3.417895000	-0.353873000
Si	-5.507719000	4.988925000	-0.339242000
C	-4.286947000	6.415797000	-0.224349000
C	-6.690788000	5.004527000	1.121688000
C	-6.452347000	5.049332000	-1.963517000
Si	4.840370000	5.015338000	0.386655000
C	3.613405000	6.437959000	0.285484000
C	6.025275000	5.051850000	-1.072381000
C	5.782501000	5.062750000	2.012919000
Si	4.875212000	-4.964854000	0.281056000
C	3.663919000	-6.391753000	0.090622000
C	5.775719000	-5.071130000	1.927984000
C	6.097138000	-4.932732000	-1.147068000
Si	-5.474277000	-4.994730000	-0.435550000
C	-4.244735000	-6.415582000	-0.341334000
C	-6.413262000	-5.032916000	-2.063777000
C	-6.662008000	-5.043271000	1.020857000
H	-1.570059000	3.398417000	-0.077964000
H	0.910531000	3.405150000	0.100207000
H	0.933410000	-3.376456000	0.037110000
H	-1.547209000	-3.383147000	-0.141285000
H	-3.576827000	6.394518000	-1.062432000

H	-4.814350000	7.380392000	-0.249973000
H	-3.712143000	6.367583000	0.710728000
H	-7.380625000	4.151048000	1.075131000
H	-7.287439000	5.928350000	1.125117000
H	-6.143759000	4.946782000	2.072445000
H	-7.042946000	5.974505000	-2.032120000
H	-5.765621000	5.017288000	-2.820195000
H	-7.139707000	4.196770000	-2.047991000
H	2.904474000	6.407040000	1.124268000
H	4.136848000	7.404503000	0.318885000
H	3.037884000	6.395515000	-0.649418000
H	6.718039000	4.200319000	-1.034787000
H	6.618551000	5.977815000	-1.064431000
H	5.479627000	5.003077000	-2.024442000
H	6.367945000	5.990290000	2.092680000
H	5.094721000	5.017311000	2.868135000
H	6.474345000	4.212998000	2.088642000
H	3.114159000	-6.317443000	-0.857699000
H	4.194583000	-7.354842000	0.101610000
H	2.931431000	-6.398346000	0.909498000
H	6.458092000	-4.219992000	2.056135000
H	6.366926000	-5.996656000	1.985545000
H	5.065971000	-5.065674000	2.766294000
H	5.575543000	-4.848053000	-2.110014000
H	6.782052000	-4.078847000	-1.056349000
H	6.697251000	-5.854195000	-1.162152000
H	-3.672885000	-6.379586000	0.596101000
H	-4.765927000	-7.382911000	-0.384768000
H	-3.532455000	-6.375645000	-1.176898000
H	-7.106219000	-4.183712000	-2.135405000
H	-6.997286000	-5.960725000	-2.150641000
H	-5.724093000	-4.981016000	-2.917513000
H	-7.253217000	-5.970469000	1.005827000
H	-6.118474000	-4.999248000	1.974351000
H	-7.356692000	-4.193128000	0.987112000

Table S3. Cartesian coordinates (XYZ) of DFT optimized geometry of **3c** (def2-TZVPP/PBE).

C	-2.847646000	1.153763000	-0.056361000
C	-1.420347000	1.230867000	-0.003899000
C	-0.704821000	0.003959000	0.018772000
C	-1.405464000	-1.231374000	-0.010485000
C	-2.833561000	-1.171169000	-0.062486000
N	-3.520566000	-0.012728000	-0.084193000
C	-0.694545000	2.455733000	0.026152000
C	0.677643000	2.463889000	0.076124000
C	1.418212000	1.247745000	0.099535000
C	0.717550000	0.012416000	0.070689000
C	1.433067000	-1.214483000	0.093212000
C	0.707272000	-2.439370000	0.062827000
C	-0.664917000	-2.447554000	0.012724000
C	2.846371000	1.187652000	0.150462000
N	3.533342000	0.029257000	0.172062000
C	2.860387000	-1.137277000	0.145313000
C	-3.622890000	2.340721000	-0.081480000
C	-3.594918000	-2.366881000	-0.094239000
C	3.635743000	-2.324102000	0.171243000
C	3.607087000	2.383901000	0.180834000
C	-4.275547000	3.374123000	-0.102719000
C	4.246225000	3.425620000	0.206206000
C	4.288920000	-3.357180000	0.192162000
C	-4.236665000	-3.406969000	-0.120989000
C	-5.052023000	4.556846000	-0.124302000
C	5.006286000	4.618677000	0.242110000
C	5.066546000	-4.539068000	0.215873000
C	-5.005385000	-4.594454000	-0.153952000
C	-6.458905000	4.496983000	-0.158162000
C	-7.219459000	5.663238000	-0.178383000
C	-6.622013000	6.932196000	-0.166565000
C	-5.216216000	6.982435000	-0.133385000
C	-4.442782000	5.830454000	-0.112407000

C	-4.393842000	-5.862805000	-0.134012000
C	-5.161877000	-7.023945000	-0.167071000
C	-6.562574000	-6.977527000	-0.221093000
C	-7.165199000	-5.706033000	-0.240633000
C	-6.415477000	-4.538842000	-0.208215000
C	6.473321000	-4.477470000	0.251276000
C	7.235215000	-5.642804000	0.273879000
C	6.639267000	-6.912478000	0.262789000
C	5.233575000	-6.964430000	0.227840000
C	4.458801000	-5.813391000	0.204620000
C	6.413856000	4.578010000	0.274477000
C	7.158109000	5.754377000	0.309541000
C	6.543074000	7.014938000	0.314355000
C	5.136712000	7.046026000	0.282422000
C	4.379374000	5.883735000	0.246721000
C	-7.430318000	8.232372000	-0.188576000
C	-8.943358000	7.978197000	-0.220524000
C	-7.102079000	9.055336000	1.074411000
C	-7.047397000	9.046129000	-1.442162000
C	-7.435101000	-8.235058000	-0.258597000
C	-6.602754000	-9.523975000	-0.229485000
C	-8.376025000	-8.236191000	0.964083000
C	-8.277687000	-8.229389000	-1.551023000
C	7.449066000	-8.211678000	0.287490000
C	8.961777000	-7.955695000	0.320362000
C	7.065903000	-9.023903000	1.541995000
C	7.122962000	-9.037009000	-0.974507000
C	7.333282000	8.325810000	0.352589000
C	8.849680000	8.092154000	0.381020000
C	6.993229000	9.159931000	-0.899920000
C	6.939629000	9.118423000	1.616354000
H	-1.255802000	3.390127000	0.008563000
H	1.227559000	3.404900000	0.098253000
H	1.268567000	-3.373748000	0.080136000
H	-1.214820000	-3.388561000	-0.010473000
H	-6.946196000	3.522286000	-0.168002000
H	-8.304164000	5.571992000	-0.204049000
H	-4.710334000	7.948830000	-0.123621000
H	-3.355218000	5.898899000	-0.086799000
H	-3.306538000	-5.927748000	-0.092158000
H	-4.648768000	-7.984170000	-0.149952000
H	-8.252163000	-5.624024000	-0.282390000
H	-6.905591000	-3.565682000	-0.224309000
H	6.959428000	-3.502178000	0.260550000
H	8.319781000	-5.550262000	0.300760000
H	4.728846000	-7.931429000	0.218372000
H	3.371355000	-5.883160000	0.177643000
H	6.914705000	3.610162000	0.271592000
H	8.243987000	5.677878000	0.333578000
H	4.617506000	8.005379000	0.285445000
H	3.290936000	5.937311000	0.222709000
H	-9.475970000	8.939154000	-0.234608000
H	-9.243877000	7.417788000	-1.116916000
H	-9.282256000	7.422522000	0.665069000
H	-7.667995000	9.998285000	1.069181000
H	-6.033960000	9.303329000	1.130837000
H	-7.368157000	8.498831000	1.983745000
H	-7.274608000	8.483214000	-2.358076000
H	-7.612238000	9.989403000	-1.468164000
H	-5.977578000	9.293038000	-1.454491000
H	-7.273392000	-10.393864000	-0.258171000
H	-5.929280000	-9.594138000	-1.095216000
H	-5.999194000	-9.599013000	0.685977000
H	-9.017498000	-9.129318000	0.946938000
H	-9.027881000	-7.352796000	0.974951000
H	-7.800743000	-8.243003000	1.900252000
H	-7.631078000	-8.231929000	-2.439446000
H	-8.918769000	-9.122180000	-1.588519000
H	-8.926369000	-7.345432000	-1.608311000
H	9.495500000	-8.916012000	0.336064000
H	9.300697000	-7.400730000	-0.565668000
H	9.260958000	-7.393813000	1.216280000
H	7.631720000	-9.966537000	1.569998000

H	5.996330000	-9.271911000	1.553688000
H	7.291660000	-8.459309000	2.457234000
H	7.389159000	-8.481600000	-1.884475000
H	7.690075000	-9.979223000	-0.967278000
H	6.055216000	-9.286463000	-1.031524000
H	9.369111000	9.060060000	0.406874000
H	9.158203000	7.524805000	1.270304000
H	9.195752000	7.552192000	-0.511487000
H	7.545947000	10.110537000	-0.882870000
H	5.921720000	9.393672000	-0.953061000
H	7.266767000	8.618669000	-1.816213000
H	7.174789000	8.547227000	2.525105000
H	7.491494000	10.068958000	1.654131000
H	5.866541000	9.350502000	1.631919000

Table S4. Cartesian coordinates (XYZ) of DFT optimized geometry of **2a** (def2-TZVPP/PBE).

C	-2.821331000	1.156453000	-0.081017000
C	-1.410020000	1.239659000	-0.019038000
C	-0.704955000	0.005083000	0.000095000
C	-1.403843000	-1.232194000	-0.048001000
C	-2.814869000	-1.154437000	-0.121419000
N	-3.491489000	-0.000316000	-0.133737000
C	-0.683464000	2.470757000	0.031849000
C	0.684184000	2.473383000	0.096821000
C	1.416888000	1.245056000	0.117485000
C	0.718003000	0.007812000	0.068168000
C	1.423086000	-1.226774000	0.085851000
C	0.696483000	-2.457917000	0.036680000
C	-0.671094000	-2.460529000	-0.029001000
C	2.828641000	1.167415000	0.177009000
N	3.504565000	0.013047000	0.201326000
C	2.833721000	-1.143791000	0.160941000
O	-3.519238000	2.310538000	-0.088421000
Si	-5.167361000	2.531505000	0.280109000
C	-5.307613000	4.398298000	0.327618000
C	-5.524959000	1.789789000	1.963154000
C	-6.269770000	1.843710000	-1.068772000
O	-3.505595000	-2.311297000	-0.180787000
Si	-5.111863000	-2.540800000	-0.695640000
C	-5.237474000	-4.408155000	-0.758483000
C	-5.321622000	-1.796998000	-2.402513000
C	-6.333698000	-1.861543000	0.550996000
O	3.530278000	-2.298290000	0.191541000
Si	5.137039000	-2.533021000	0.702386000
C	5.271395000	-4.400742000	0.719230000
C	5.341178000	-1.830280000	2.427257000
C	6.357334000	-1.817326000	-0.525167000
O	3.520798000	2.324413000	0.211799000
Si	5.168571000	2.562081000	-0.147888000
C	5.300048000	4.430117000	-0.149151000
C	5.532429000	1.863561000	-1.847935000
C	6.271540000	1.846162000	1.185798000
H	-1.244477000	3.403952000	0.016131000
H	1.240514000	3.408712000	0.135390000
H	1.257560000	-3.391088000	0.051366000
H	-1.227496000	-3.395851000	-0.066700000
H	-5.043011000	4.838263000	-0.644009000
H	-6.335583000	4.705563000	0.568197000
H	-4.639159000	4.825422000	1.087773000
H	-5.288259000	0.718753000	1.986527000
H	-6.585659000	1.913460000	2.225724000
H	-4.925261000	2.289744000	2.736792000
H	-7.312407000	2.151073000	-0.899110000

H	-5.962548000	2.229124000	-2.051342000
H	-6.234478000	0.749171000	-1.104966000
H	-5.056831000	-4.848624000	0.231976000
H	-6.238942000	-4.719854000	-1.088546000
H	-4.502998000	-4.830797000	-1.457781000
H	-5.094893000	-0.723542000	-2.400523000
H	-6.351850000	-1.930726000	-2.763055000
H	-4.647376000	-2.287731000	-3.118578000
H	-7.357254000	-2.161695000	0.281700000
H	-6.121332000	-2.257025000	1.554397000
H	-6.297094000	-0.767510000	0.600482000
H	5.094163000	-4.817381000	-0.282098000
H	6.273894000	-4.715805000	1.042911000
H	4.538000000	-4.844035000	1.406772000
H	5.108205000	-0.758411000	2.451460000
H	6.371903000	-1.966731000	2.785351000
H	4.669276000	-2.342366000	3.130455000
H	7.381877000	-2.119353000	-0.261782000
H	6.148346000	-2.188525000	-1.538499000
H	6.315616000	-0.722573000	-0.547264000
H	5.032393000	4.844785000	0.832710000
H	6.326804000	4.748003000	-0.380970000
H	4.630362000	4.872695000	-0.899315000
H	5.299440000	0.792624000	-1.898073000
H	6.593204000	1.997339000	-2.105178000
H	4.932491000	2.380391000	-2.610217000
H	7.312847000	2.163551000	1.026768000
H	5.959757000	2.204497000	2.177138000
H	6.242233000	0.750875000	1.193741000

Table S5. Cartesian coordinates (XYZ) of DFT optimized geometry of **3a** (def2-TZVPP/PBE).

C	-2.917659000	1.065056000	0.437151000
C	-1.498826000	1.184916000	0.519839000
C	-0.744149000	-0.023963000	0.474511000
C	-1.406543000	-1.285791000	0.473816000
C	-2.829328000	-1.265593000	0.430819000
N	-3.531673000	-0.127716000	0.414754000
C	-0.808621000	2.410684000	0.773656000
C	0.558991000	2.458819000	0.821276000
C	1.347760000	1.286026000	0.614183000
C	0.687954000	0.027149000	0.510316000
C	1.441399000	-1.183297000	0.521888000
C	0.741455000	-2.420717000	0.670815000
C	-0.626822000	-2.469639000	0.650082000
C	2.770964000	1.266567000	0.638207000
N	3.475016000	0.130644000	0.591019000
C	2.862431000	-1.060698000	0.515087000
N	-3.734095000	2.196677000	0.403952000
N	-3.555538000	-2.465658000	0.412562000
N	3.681306000	-2.189484000	0.456931000
N	3.495129000	2.464966000	0.723301000
C	-5.156189000	2.032925000	0.709631000
C	-6.014419000	1.743225000	-0.526026000
C	-5.788544000	2.813755000	-1.596931000
C	-4.294638000	2.958917000	-1.896323000
C	-3.495119000	3.226599000	-0.614404000
C	-4.970423000	-2.389790000	0.770456000
C	-5.484521000	-3.777319000	1.154191000
C	-5.253212000	-4.788725000	0.028746000
C	-3.783831000	-4.782154000	-0.400840000
C	-3.330696000	-3.363107000	-0.729314000
C	5.086543000	-2.045342000	0.840419000
C	6.003403000	-1.686371000	-0.333431000
C	5.831775000	-2.693707000	-1.473445000
C	4.354468000	-2.820006000	-1.853072000
C	3.493776000	-3.159261000	-0.629036000

C	4.891187000	2.367670000	1.144462000
C	5.383380000	3.730671000	1.630977000
C	5.205409000	4.804557000	0.554807000
C	3.758810000	4.823723000	0.054289000
C	3.324181000	3.426069000	-0.375353000
H	-1.389090000	3.303659000	1.000723000
H	1.061454000	3.388485000	1.085654000
H	1.311459000	-3.326270000	0.873246000
H	-1.139759000	-3.412531000	0.835751000
H	-5.256282000	1.232365000	1.450462000
H	-5.493156000	2.977236000	1.174347000
H	-5.736284000	0.752314000	-0.915017000
H	-7.075106000	1.699930000	-0.234015000
H	-6.346032000	2.571795000	-2.513938000
H	-6.179809000	3.781681000	-1.236162000
H	-3.916403000	2.033164000	-2.360059000
H	-4.114209000	3.776760000	-2.611303000
H	-2.425169000	3.271419000	-0.840582000
H	-3.787442000	4.204460000	-0.191870000
H	-5.077691000	-1.684224000	1.602471000
H	-5.569096000	-1.982546000	-0.070749000
H	-4.960092000	-4.109632000	2.064337000
H	-6.554855000	-3.709426000	1.400626000
H	-5.564255000	-5.796634000	0.340609000
H	-5.881009000	-4.516075000	-0.837109000
H	-3.154796000	-5.178600000	0.412791000
H	-3.629905000	-5.427042000	-1.279030000
H	-2.271320000	-3.337316000	-1.005948000
H	-3.905051000	-2.988617000	-1.604719000
H	5.149240000	-1.288641000	1.629833000
H	5.401824000	-3.015156000	1.266203000
H	5.742752000	-0.674566000	-0.678195000
H	7.048551000	-1.660914000	0.011847000
H	6.432780000	-2.400339000	-2.346925000
H	6.206768000	-3.681027000	-1.149886000
H	3.997592000	-1.869039000	-2.281342000
H	4.210516000	-3.595703000	-2.621312000
H	2.436214000	-3.189401000	-0.909403000
H	3.766423000	-4.160105000	-0.249348000
H	4.959315000	1.615724000	1.939158000
H	5.530815000	2.008656000	0.311478000
H	4.814616000	4.011317000	2.531847000
H	6.440547000	3.647860000	1.925085000
H	5.498739000	5.792862000	0.938367000
H	5.875553000	4.581503000	-0.293337000
H	3.090298000	5.174733000	0.857245000
H	3.646809000	5.517143000	-0.792725000
H	2.279386000	3.417593000	-0.703620000
H	3.940370000	3.101071000	-1.242049000

TD-DFT calculations

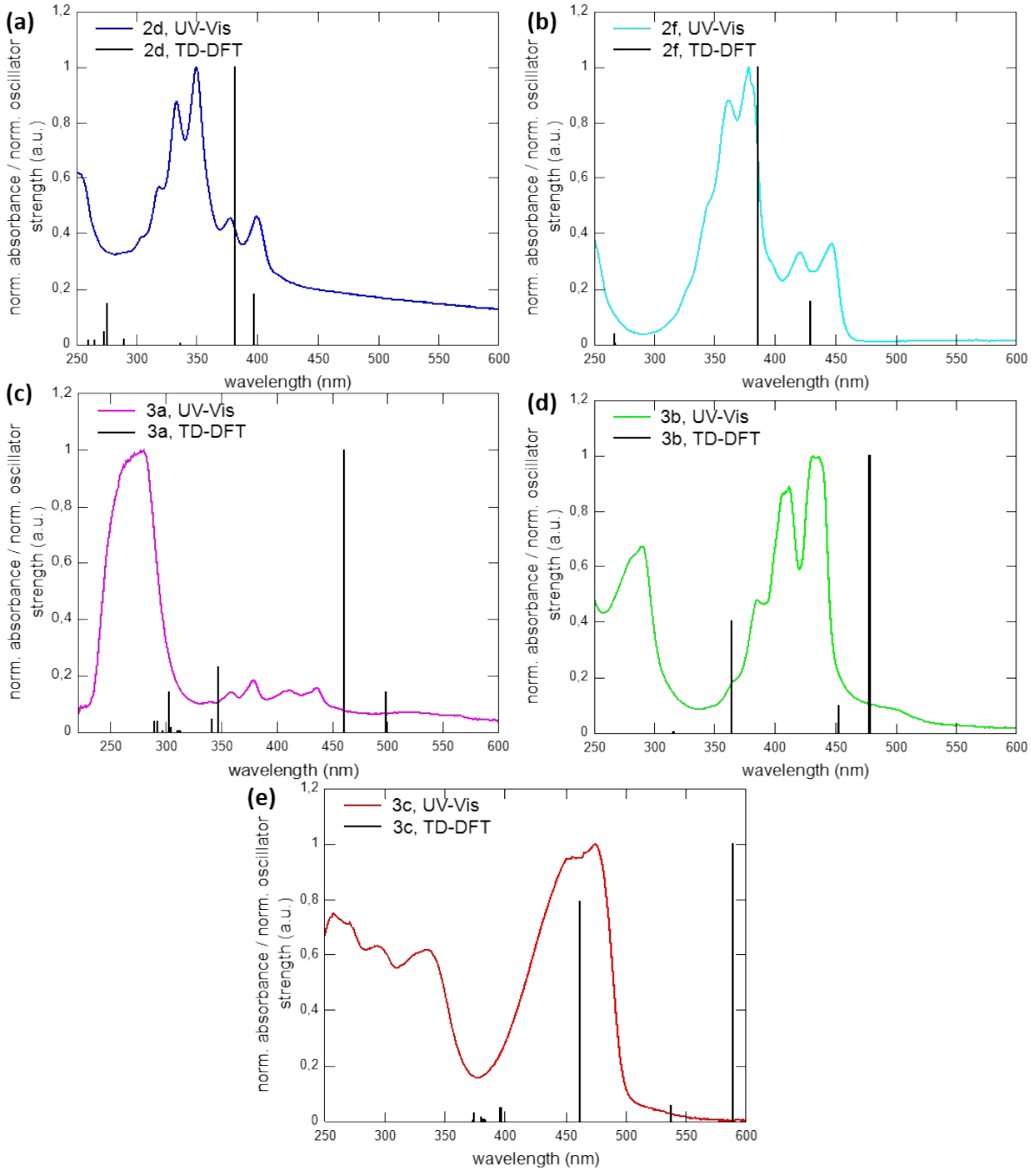


Figure S2. Comparison of normalized UV-Vis spectra (recorded in CH_2Cl_2) and normalized electron transitions calculated by TD-DFT (black bars, def2-TZVPP/PBE level of theory) of a) **2d** (calculation for silyl ether **2a**); b) of **2f**; c) of **3a**; d) of **3b**; e) of **3c**.

Table S6. Characteristic main electron transition of **2a**, **2f**, **3a**, **3b** and **3c** calculated using TD-DFT (def2-TZVPP/PBE level of theory).

Compound	Transition energy (wavelength)	Oscillator strength	Description of main contributions
2a	2.88 eV (429 nm)	0.119	HOMO→LUMO+1 (c = -0.950); 0.903 HOMO-1→LUMO+2 (c = -0.152); 0.023 HOMO-4→LUMO (c = -0.210 0.045
	3.22 eV (385 nm)	0.768	HOMO→LUMO (c = 0.927); 0.859 HOMO-1→LUMO+3 (c = -0.105); 0.011 HOMO-2→LUMO+2 (c = 0.177); 0.031 HOMO-4→LUMO+1 (c = -0.241); 0.058
2d	3.13 eV (397 nm)	0.119	HOMO→LUMO+1 (c = -0.937); 0.877 HOMO-3→LUMO+1 (c = -0.107); 0.011 HOMO-5→LUMO (c = -0.282); 0.080
	3.26 eV (381 nm)	0.652	HOMO→LUMO (c = 0.922); 0.849 HOMO-2→LUMO+2 (c = -0.165); 0.027 HOMO-5→LUMO+1 (c = -0.266); 0.071
3a	2.49 eV (498 nm)	0.115	HOMO→LUMO (c = 0.246); 0.059 HOMO→LUMO+1 (c = 0.916); 0.839 HOMO-1→LUMO+2 (c = -0.134); 0.018 HOMO-3→LUMO (c = 0.196); 0.038 HOMO-8→LUMO (c = 0.112); 0.012
	2.69 eV (460 nm)	0.818	HOMO→LUMO (c = -0.913); 0.833 HOMO→LUMO+1 (c = 0.239); 0.057 HOMO-7→LUMO+2 (c = -0.114); 0.013 HOMO-8→LUMO (c = -0.114); 0.020 HOMO-9→LUMO+1 (c = -0.168); 0.028
3b	2.59 eV (478 nm)	1.115	HOMO→LUMO (c = -0.959); 0.902 HOMO-11→LUMO+1 (c = 0.149); 0.022 HOMO-12→LUMO (c = 0.149); 0.022
3c	2.14 eV (579 nm)	1.632	HOMO→LUMO (c = -0.960); 0.921 HOMO-6→LUMO (c = 0.170); 0.028

Concentration-dependent UV-Vis spectroscopy

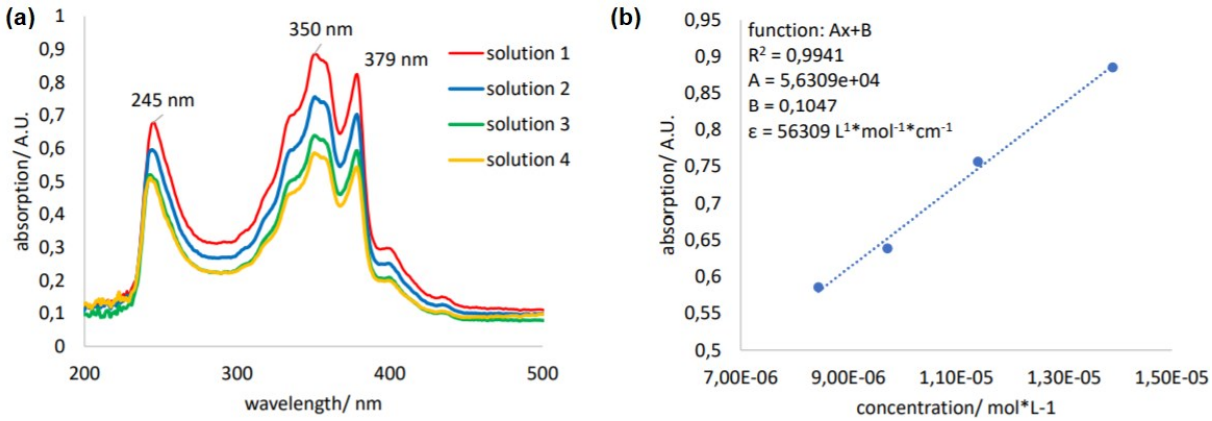


Figure S3. a) UV-Vis spectra of **2d** in dichloromethane in four different concentrations; b) corresponding linear regression of the absorbances for the determination of the molar decadic attenuation coefficient (ε).

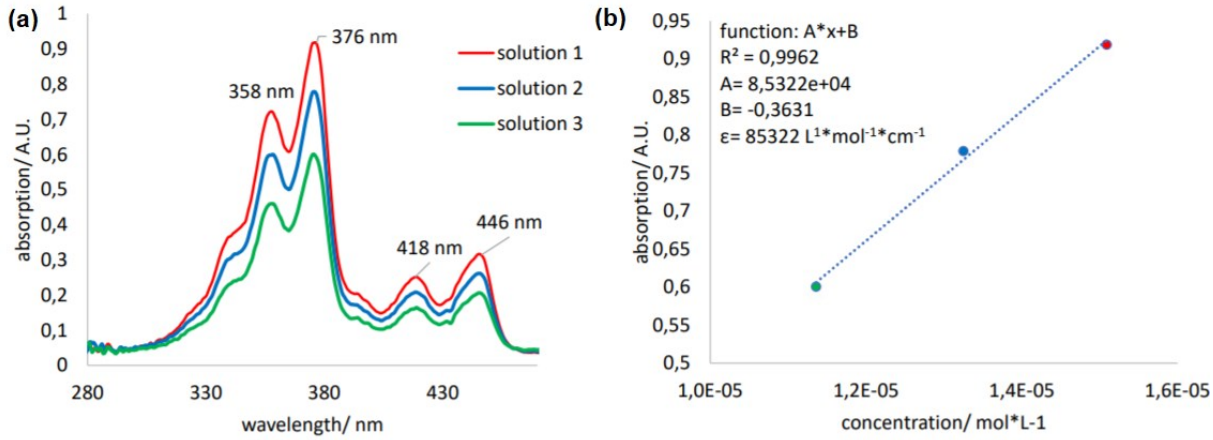


Figure S4. a) UV-Vis spectra of **2f** in dichloromethane in four different concentrations; b) corresponding linear regression of the absorbances for the determination of the molar decadic attenuation coefficient (ε).

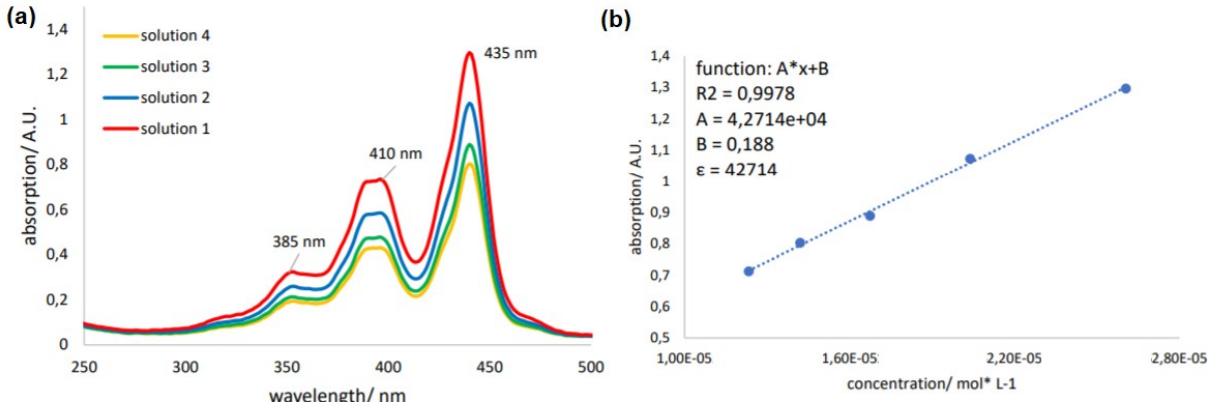


Figure S5. a) UV-Vis spectra of **3b** in dichloromethane in four different concentrations; b) corresponding linear regression of the absorbances for the determination of the molar decadic attenuation coefficient (ε).

UV-Vis spectra in different solvents

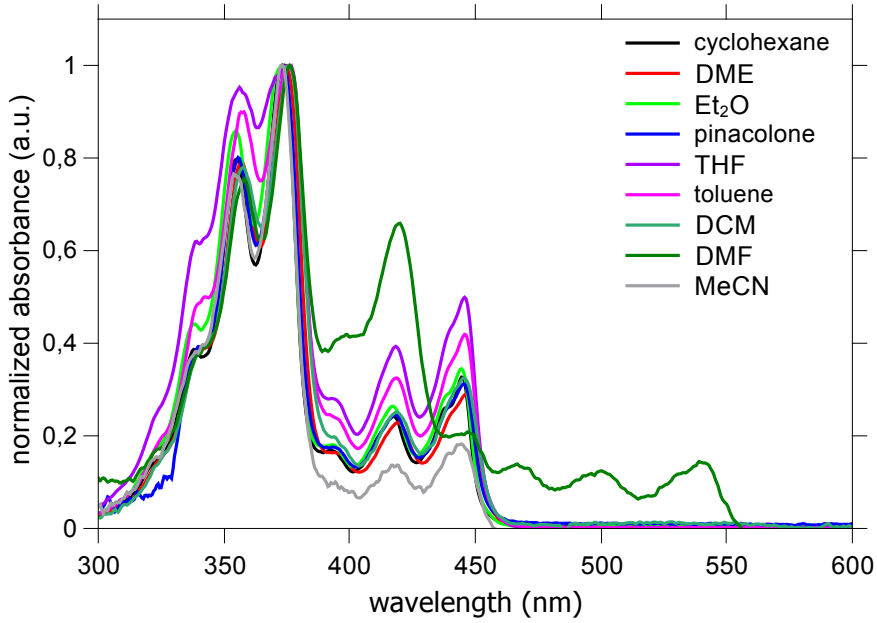


Figure S6. a) Normalized UV-Vis spectra of **2f** recorded in different solvents (c ≈ 10^{-5} M). Note that **2f** decomposes in DMF.

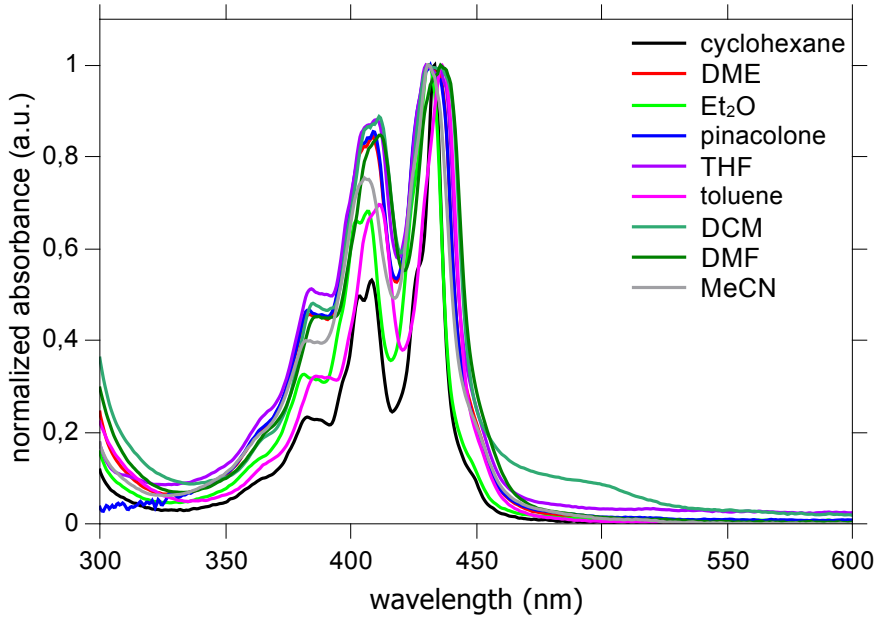


Figure S7. a) Normalized UV-Vis spectra of **3b** recorded in different solvents (c ≈ 10^{-5} M).

Determination of fluorescence quantum yields

Fluorescence quantum yields (Φ_{PL}) were recorded by dilution method using a fluorescein solution (0.1 M in aqueous NaOH, Φ_{flu} = 0.95[1]) as reference. Both, the samples and the reference were measured at low concentrations in order to ensure a linear relationship between the intensity of emitted light and the concentration of the absorbing/emitting species.
The quantum yields of the samples (Φ_s) were determined by the following equation 1.[1]

$$\Phi_{flu} = \frac{grad\,(s)}{grad\,(flu)} * \frac{n^2(s)}{n^2(flu)} * \Phi_{flu}$$

In equation 1, *grad* is the slope of the "emission versus absorbance" plot of the samples (s) and the standard fluorescein (flu). n is the refractive index of the used solvents.
In the following Figure S7, the "emission versus absorbance" plots and the linear regression graphs for the determination of the fluorescence quantum yields of **2d**, **2f**, **3b**, **3c** as well as the reference fluorescein are shown.

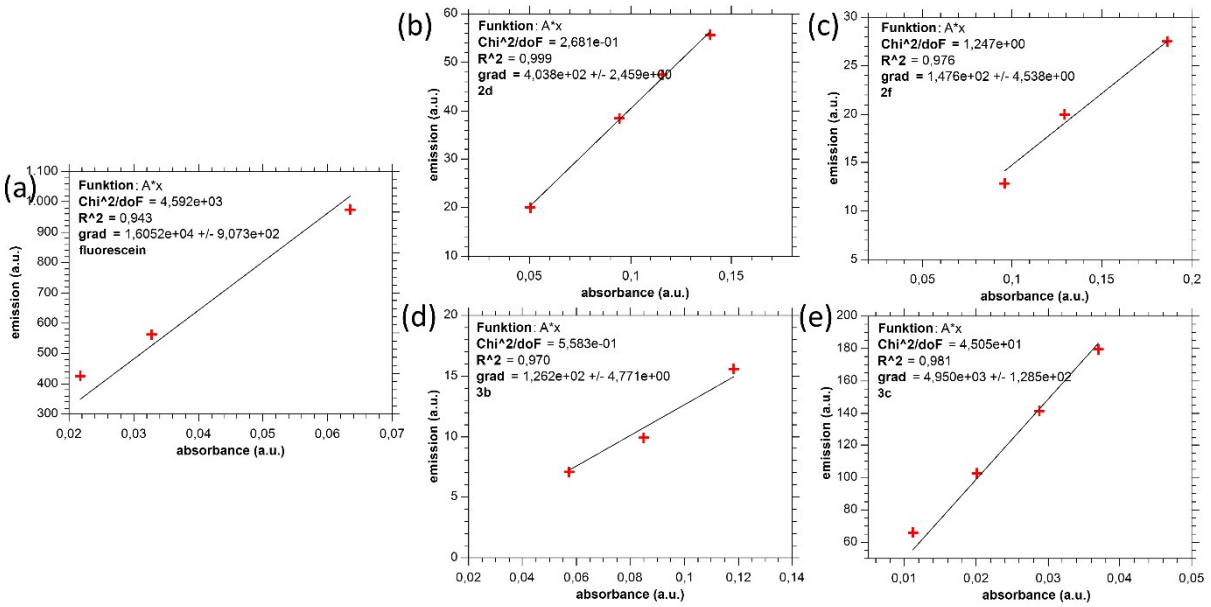


Figure S8. "Emission versus absorption" plots of (a) fluorescein (in 0.1 M NaOH solution); (b) **2d**; (c) **2f**; (d) **3b**; (e) **3c** recorded in dichloromethane. The concentrations were in the low 10^{-6} M range.

1 J. R. Lakowicz, *Principles of fluorescence spectroscopy*, Springer, New York, NY, 4th edn., 2010.

Single crystal X-ray structures

Crystal Data

	1,3,6,8-Tetrakis((trimethylsilyl)oxy)benzo[lmn][3,8]phenanthroline (2a)	1,3,6,8-Tetrakis((tert-butyldimethylsilyl)oxy)benzo[lmn][3,8]phenanthroline (2f)	1,3,6,8-Tetrakis((trimethylsilyl)ethynyl)benzo[lmn][3,8]phenanthroline (3b)
CCDC code	2087066	2087065	2087067
Identification code	swp213loesen	kbv4loesen	swp162gloesen
Empirical formula	$C_{26}H_{40}N_2O_4Si_4$	$C_{42}H_{72}N_2O_6Si_4$	$C_{18}H_{21}Cl_3NSi_2$
Formula weight	556.96 g/mol	813.37 g/mol	413.89 g/mol
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	1.54186 Å	1.54186 Å	1.54186 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	*P-1*	$P2_1/n$
Unit cell dimensions	a = 11.258(2) Å	a = 7.8672(2) Å	a = 6.3490(13) Å
	b = 11.167(2) Å	b = 11.2136(3) Å	b = 22.215(4) Å
	c = 13.919(3) Å	c = 13.7228(3) Å	c = 15.599(3) Å
	α = 90°.	α = 95.577(2)°.	α = 90°.
	β = 113.25(3)°	β = 100.951(2)°	β = 101.54(3)°
	γ = 90°.	γ = 96.686(2)°	γ = 90°.
Volume	1607.7(6) Å^3	2893.0(4) Å^3	2155.7(8) Å^3
Z	2	1	4
Density (calculated)	1.151 g/cm^3	1.153 g/cm^3	1.275 g/cm^3
Absorption coefficient	1.966 mm^{-1}	1.525 mm^{-1}	4.911 mm^{-1}
F(000)	596	422	860
Crystal size	0.307x0.169x0.074 mm^3	0.235x0.168x0.110 mm^3	0.307x 0.169x0.074 mm^3
Theta range for data collection	3.979 to 69.993°	3.999 to 66.493°	3.510 to 66.595°
Index ranges	*h* = -13 ↔ 13, *k* = -12 ↔ 13, *l* = -16 ↔ 13	*h* = -16 ↔ 16, *k* = -18 ↔ 16, *l* = -17 ↔ 18	*h* = -7 ↔ 7, *k* = -26 ↔ 26, *l* = -18 ↔ 9
Reflections collected	56597	19390	23677
Independent reflections	34488 [R(int) = 0.0341]	4077 [R(int) = 0.0292]	3803 [R(int) = 0.0482]
Completeness to theta = x	100% (x= 66.45°)	95.5% (x= 66.50°)	99.4% (x= 66.60°)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.1859 and 0.3540	0.2514 and 0.6611	0.3254 and 1.0000
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	56597 / 0 / 171	4077 / 0 / 254	3803 / 0 / 223
Goodness-of-fit on F^2	1.026	1.067	1.056
Final R indices [I>2sigma(I)]	R_1 = 0.0718, wR_2 = 0.2146	R_1 = 0.0459, wR_2 = 0.1303	R_1 = 0.0474, wR_2 = 0.1311
R indices (all data)	R_1 = 0.0994, wR_2 = 0.2526	R_1 = 0.0491, wR_2 = 0.1328	R_1 = 0.0555, wR_2 = 0.1376
Extinction coefficient	n/a	n/a	n/a
Largest diff. peak and hole	0.560 and -0.416 e·Å^{-3}	0.214 and -0.370 e·Å^{-3}	0.374 and -0.476 e·Å^{-3}

Molecular structures of the title compounds

1,3,6,8-Tetrakis((trimethylsilyl)oxy)benzo[lmn][3,8]phenanthroline (**2a**)

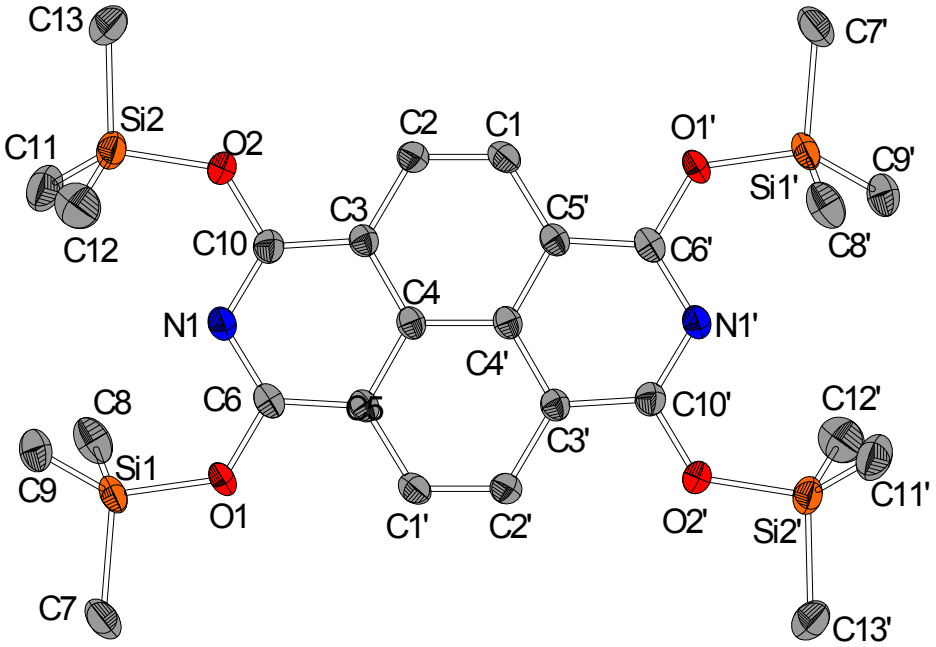


Figure S9. Reduced cell of the crystallographically determined molecular structure of **2a**. Protons are not shown. Symmetry transformations: 2 -x, 1-y, 1-z.

Table S7. Bond lengths [Å] and angles [°] **2a**.

Si(1)-O(1)	1.685(3)
Si(1)-C(8)	1.847(5)
Si(1)-C(7)	1.848(4)
Si(1)-C(9)	1.848(4)
Si(2)-O(2)	1.675(3)
Si(2)-C(11)	1.849(5)
Si(2)-C(12)	1.849(5)
Si(2)-C(13)	1.855(4)
O(1)-C(6)	1.348(4)
O(2)-C(10)	1.350(4)
N(1)-C(10)	1.333(4)
N(1)-C(6)	1.339(5)
C(1)-C(2)	1.350(5)
C(1)-C(5)#1	1.436(5)
C(2)-C(3)	1.437(5)
C(3)-C(10)	1.405(5)
C(3)-C(4)	1.410(5)
C(4)-C(5)	1.413(5)
C(4)-C(4)#1	1.425(6)
C(5)-C(6)	1.404(5)
O(1)-Si(1)-C(8)	108.87(16)
O(1)-Si(1)-C(7)	103.08(17)
C(8)-Si(1)-C(7)	111.4(2)
O(1)-Si(1)-C(9)	111.28(18)
C(8)-Si(1)-C(9)	111.9(2)
C(7)-Si(1)-C(9)	109.97(19)
O(2)-Si(2)-C(11)	109.59(18)
O(2)-Si(2)-C(12)	109.6(2)
C(11)-Si(2)-C(12)	113.6(2)

O(2)-Si(2)-C(13)	101.39(17)
C(11)-Si(2)-C(13)	111.4(2)
C(12)-Si(2)-C(13)	110.6(2)
C(6)-O(1)-Si(1)	128.3(3)
C(10)-O(2)-Si(2)	130.1(2)
C(10)-N(1)-C(6)	118.1(3)
C(2)-C(1)-C(5)#1	121.0(3)
C(1)-C(2)-C(3)	120.5(3)
C(10)-C(3)-C(4)	116.2(3)
C(10)-C(3)-C(2)	123.9(3)
C(4)-C(3)-C(2)	119.8(3)
C(3)-C(4)-C(5)	120.8(3)
C(3)-C(4)-C(4)#1	119.5(4)
C(5)-C(4)-C(4)#1	119.7(4)
C(6)-C(5)-C(4)	116.3(3)
C(6)-C(5)-C(1)#1	124.2(3)
C(4)-C(5)-C(1)#1	119.4(3)
N(1)-C(6)-O(1)	118.3(3)
N(1)-C(6)-C(5)	124.1(3)
O(1)-C(6)-C(5)	117.5(3)
N(1)-C(10)-O(2)	118.5(3)
N(1)-C(10)-C(3)	124.4(3)
O(2)-C(10)-C(3)	117.0(3)

Symmetry transformations used to generate equivalent atoms:
#2 -x, 1-y, 1-z.

1,3,6,8-Tetrakis((tert-butyldimethylsilyl)oxy)benzo[lmn][3,8]phenanthroline (**2f**)

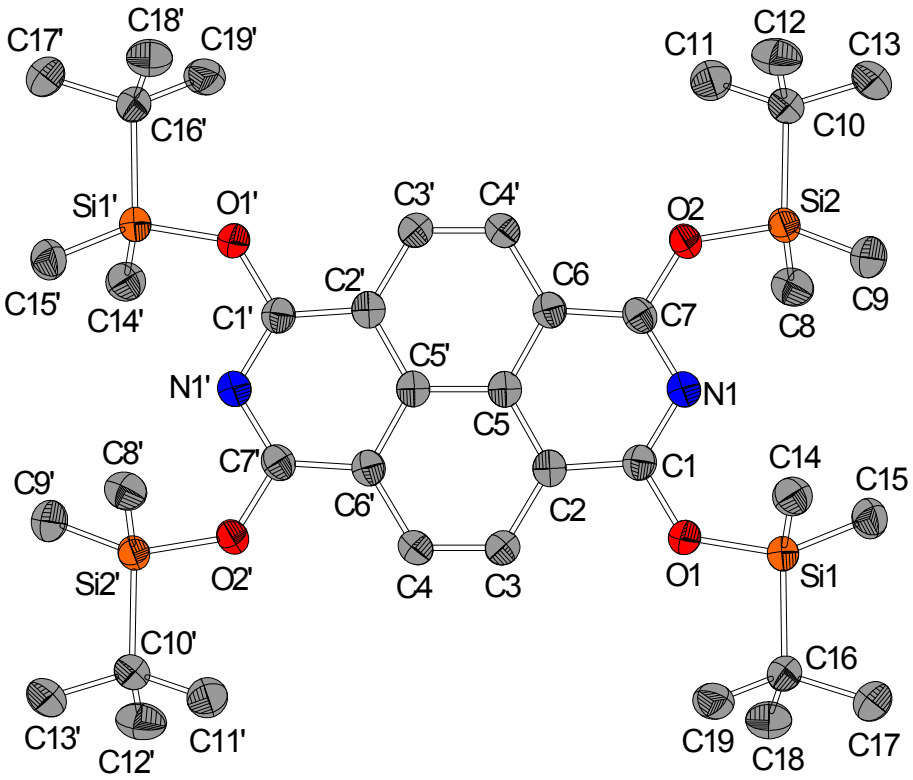


Figure S10. Reduced cell of the crystallographically determined molecular structure of **2f**. Protons are not shown. Symmetry transformations: 1 -x+1,-y+1,-z+1 and 2 -x+2,-y,-z+1.

Table S8. Bond lengths [Å] and angles [°] **2f**.

Si(1)-O(1)	1.6809(12)
Si(1)-C(14)	1.8536(19)
Si(1)-C(15)	1.8588(18)
Si(1)-C(16)	1.8741(18)
Si(2)-O(2)	1.6824(12)
Si(2)-C(8)	1.8516(19)
Si(2)-C(9)	1.8543(18)
Si(2)-C(10)	1.8753(18)
O(1)-C(1)	1.357(2)
O(2)-C(7)	1.353(2)
O(3)-C(21)	1.378(3)
O(3)-C(20)	1.439(3)
N(1)-C(1)	1.331(2)
N(1)-C(7)	1.337(2)
C(1)-C(2)	1.406(2)
C(2)-C(5)	1.412(2)
C(2)-C(3)	1.433(2)
C(3)-C(4)	1.356(2)
C(4)-C(6)#1	1.435(2)
C(5)-C(6)	1.413(2)
C(5)-C(5)#1	1.431(3)
C(6)-C(7)	1.404(2)
C(10)-C(12)	1.536(3)
C(10)-C(13)	1.538(2)
C(10)-C(11)	1.539(3)
C(16)-C(17)	1.533(2)
C(16)-C(18)	1.536(3)
C(16)-C(19)	1.538(2)
C(20)-C(21)#2	1.526(3)
O(1)-Si(1)-C(14)	110.39(8)
O(1)-Si(1)-C(15)	110.90(8)
C(14)-Si(1)-C(15)	110.56(9)
O(1)-Si(1)-C(16)	102.18(7)
C(14)-Si(1)-C(16)	111.32(9)
C(15)-Si(1)-C(16)	111.23(9)
O(2)-Si(2)-C(8)	108.67(7)
O(2)-Si(2)-C(9)	109.94(8)
C(8)-Si(2)-C(9)	111.91(9)
O(2)-Si(2)-C(10)	103.12(7)
C(8)-Si(2)-C(10)	111.37(9)
C(9)-Si(2)-C(10)	111.44(9)
C(1)-O(1)-Si(1)	128.80(11)
C(7)-O(2)-Si(2)	125.81(11)
C(21)-O(3)-C(20)	111.67(18)
C(1)-N(1)-C(7)	118.04(14)
N(1)-C(1)-O(1)	117.65(14)
N(1)-C(1)-C(2)	124.66(16)
O(1)-C(1)-C(2)	117.69(15)
C(1)-C(2)-C(5)	115.78(16)
C(1)-C(2)-C(3)	124.34(16)
C(5)-C(2)-C(3)	119.84(15)
C(4)-C(3)-C(2)	120.62(16)
C(3)-C(4)-C(6)#1	120.77(16)
C(2)-C(5)-C(6)	121.09(16)
C(2)-C(5)-C(5)#1	119.64(19)
C(6)-C(5)-C(5)#1	119.3(2)
C(7)-C(6)-C(5)	116.05(16)
C(7)-C(6)-C(4)#1	124.09(16)
C(5)-C(6)-C(4)#1	119.85(15)
N(1)-C(7)-O(2)	117.54(14)

N(1)-C(7)-C(6)	124.32(16)
O(2)-C(7)-C(6)	118.15(16)
C(12)-C(10)-C(13)	109.35(16)
C(12)-C(10)-C(11)	108.90(17)
C(13)-C(10)-C(11)	108.57(16)
C(12)-C(10)-Si(2)	109.84(13)
C(13)-C(10)-Si(2)	109.99(13)
C(11)-C(10)-Si(2)	110.16(13)
C(17)-C(16)-C(18)	108.76(16)
C(17)-C(16)-C(19)	108.92(16)
C(18)-C(16)-C(19)	108.38(15)
C(17)-C(16)-Si(1)	109.57(13)
C(18)-C(16)-Si(1)	110.75(13)
C(19)-C(16)-Si(1)	110.42(12)
O(3)-C(20)-C(21)#2	111.18(18)
O(3)-C(21)-C(20)#2	109.81(18)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x+2,-y,-z+1

1,3,6,8-Tetrakis((trimethylsilyl)ethynyl)benzo[lmn][3,8]phenanthroline (3b)

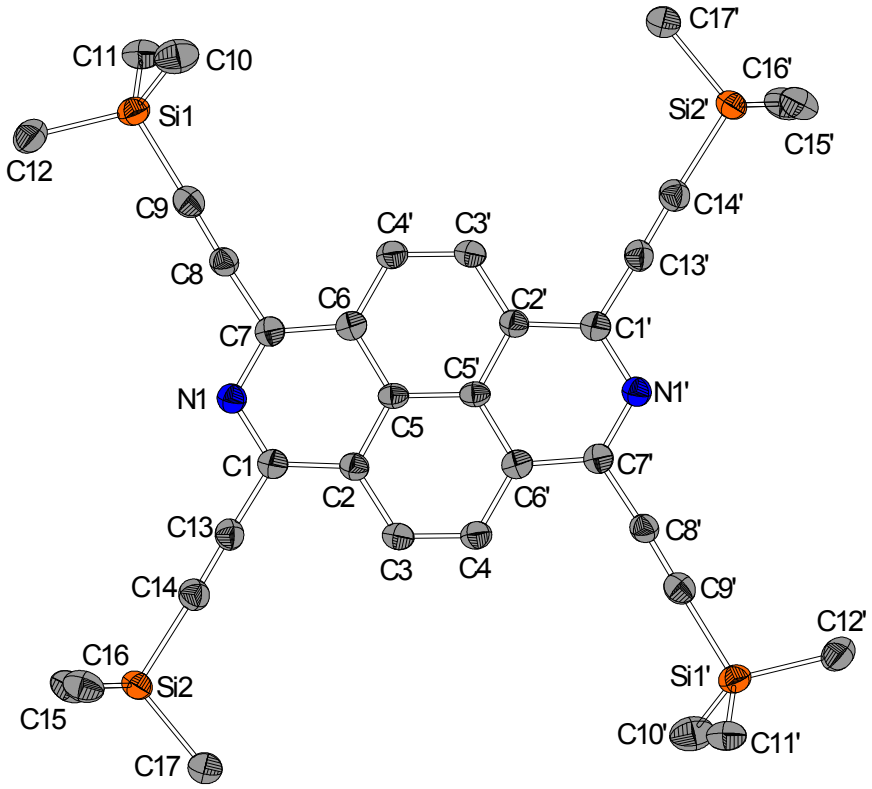


Figure S11. Reduced cell of the crystallographically determined molecular structure of **3b**. Protons are not shown. Symmetry transformations: 2-x, 1-y, 1-z.

Table S9. Bond lengths [Å] and angles [°] **3b**.

C(1)-N(1)	1.341(3)
C(1)-C(2)	1.414(3)
C(1)-C(13)	1.438(4)
C(2)-C(5)	1.411(3)
C(2)-C(3)	1.428(4)
C(3)-C(4)	1.360(4)

C(3)-H(3)	0.9300
C(4)-C(6)#1	1.426(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.418(3)
C(5)-C(5)#1	1.420(5)
C(6)-C(7)	1.414(3)
C(7)-N(1)	1.349(3)
C(7)-C(8)	1.442(4)
C(8)-C(9)	1.207(4)
C(9)-Si(1)	1.844(3)
C(10)-Si(1)	1.862(3)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-Si(1)	1.862(3)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-Si(1)	1.859(3)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-C(14)	1.212(4)
C(14)-Si(2)	1.850(3)
C(15)-Si(2)	1.856(3)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-Si(2)	1.858(3)
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-Si(2)	1.862(3)
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-Cl(3)	1.746(3)
C(18)-Cl(1)	1.760(3)
C(18)-Cl(2)	1.763(3)
C(18)-H(18)	0.9800

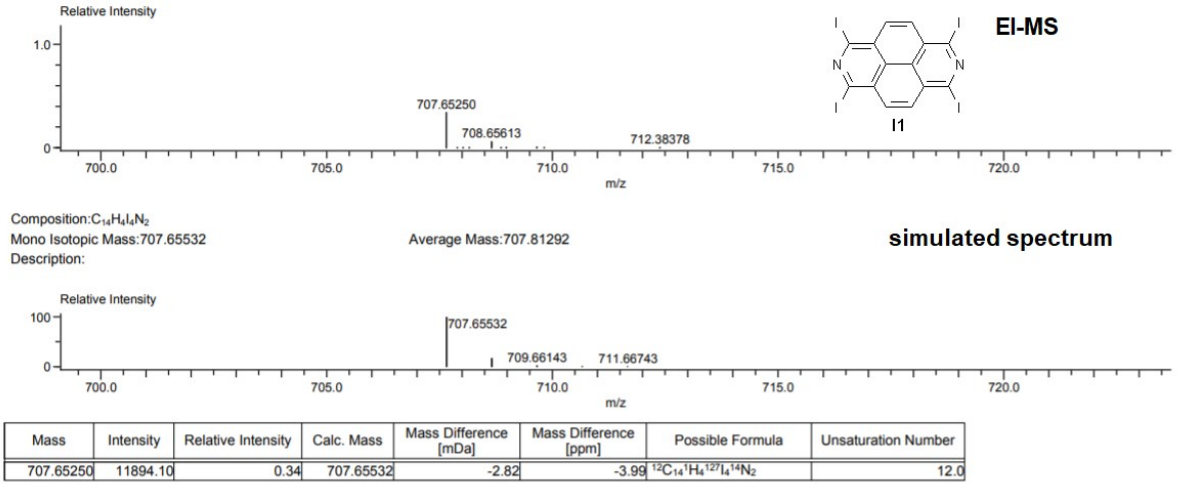
N(1)-C(1)-C(2)	123.5(2)
N(1)-C(1)-C(13)	116.6(2)
C(2)-C(1)-C(13)	119.9(2)
C(5)-C(2)-C(1)	117.3(2)
C(5)-C(2)-C(3)	119.0(2)
C(1)-C(2)-C(3)	123.7(2)
C(4)-C(3)-C(2)	121.1(2)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(6)#1	121.0(2)
C(3)-C(4)-H(4)	119.5
C(6)#1-C(4)-H(4)	119.5
C(2)-C(5)-C(6)	120.2(2)
C(2)-C(5)-C(5)#1	120.3(3)
C(6)-C(5)-C(5)#1	119.5(3)
C(7)-C(6)-C(5)	116.7(2)
C(7)-C(6)-C(4)#1	124.1(2)
C(5)-C(6)-C(4)#1	119.2(2)
N(1)-C(7)-C(6)	123.8(2)
N(1)-C(7)-C(8)	117.3(2)
C(6)-C(7)-C(8)	119.0(2)
C(9)-C(8)-C(7)	177.0(3)

C(8)-C(9)-Si(1)	177.5(2)
Si(1)-C(10)-H(10A)	109.5
Si(1)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
Si(1)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
Si(1)-C(11)-H(11A)	109.5
Si(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
Si(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
Si(1)-C(12)-H(12A)	109.5
Si(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
Si(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(1)	177.9(3)
C(13)-C(14)-Si(2)	175.2(2)
Si(2)-C(15)-H(15A)	109.5
Si(2)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
Si(2)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
Si(2)-C(16)-H(16A)	109.5
Si(2)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
Si(2)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
Cl(3)-C(18)-Cl(1)	110.95(16)
Cl(3)-C(18)-Cl(2)	110.02(15)
Cl(1)-C(18)-Cl(2)	110.40(16)
Cl(3)-C(18)-H(18)	108.5
Cl(1)-C(18)-H(18)	108.5
Cl(2)-C(18)-H(18)	108.5
C(1)-N(1)-C(7)	118.5(2)
C(9)-Si(1)-C(12)	108.22(13)
C(9)-Si(1)-C(10)	107.27(14)
C(12)-Si(1)-C(10)	112.25(16)
C(9)-Si(1)-C(11)	109.51(13)
C(12)-Si(1)-C(11)	109.35(15)
C(10)-Si(1)-C(11)	110.17(14)
C(14)-Si(2)-C(15)	109.46(13)
C(14)-Si(2)-C(16)	106.79(13)
C(15)-Si(2)-C(16)	111.22(14)
C(14)-Si(2)-C(17)	108.43(13)
C(15)-Si(2)-C(17)	109.12(14)
C(16)-Si(2)-C(17)	111.75(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1

EI-MS spectrum of 1,3,6,8-tetraiodobenzo[lmn][3,8]phenanthroline (I1)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
707.65250	11894.10	0.34	707.65532	-2.82	-3.99	$^{12}C_{14}{}^{1}H_{4}{}^{127}I_{4}{}^{14}N_{2}$	12.0

Figure S12. High-resolution electron ionization (EI) mass spectrum (top) of **I1** and simulated spectrum (below).

NMR spectra

*1,3,6,8-Tetrakis((trimethylsilyl)oxy)benzo[lmn][3,8]phenanthroline (**2a**)*

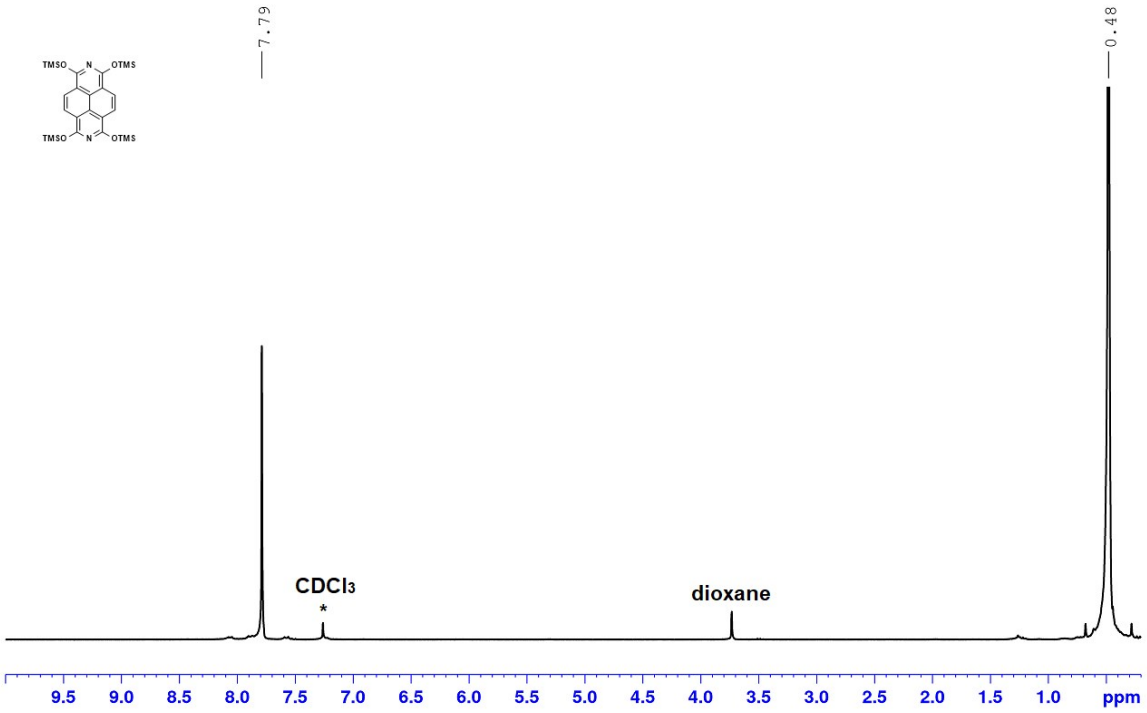


Figure S13. ^{1}H-NMR (300.1 MHz, 298K, $CDCl_3$*) of **2a**.

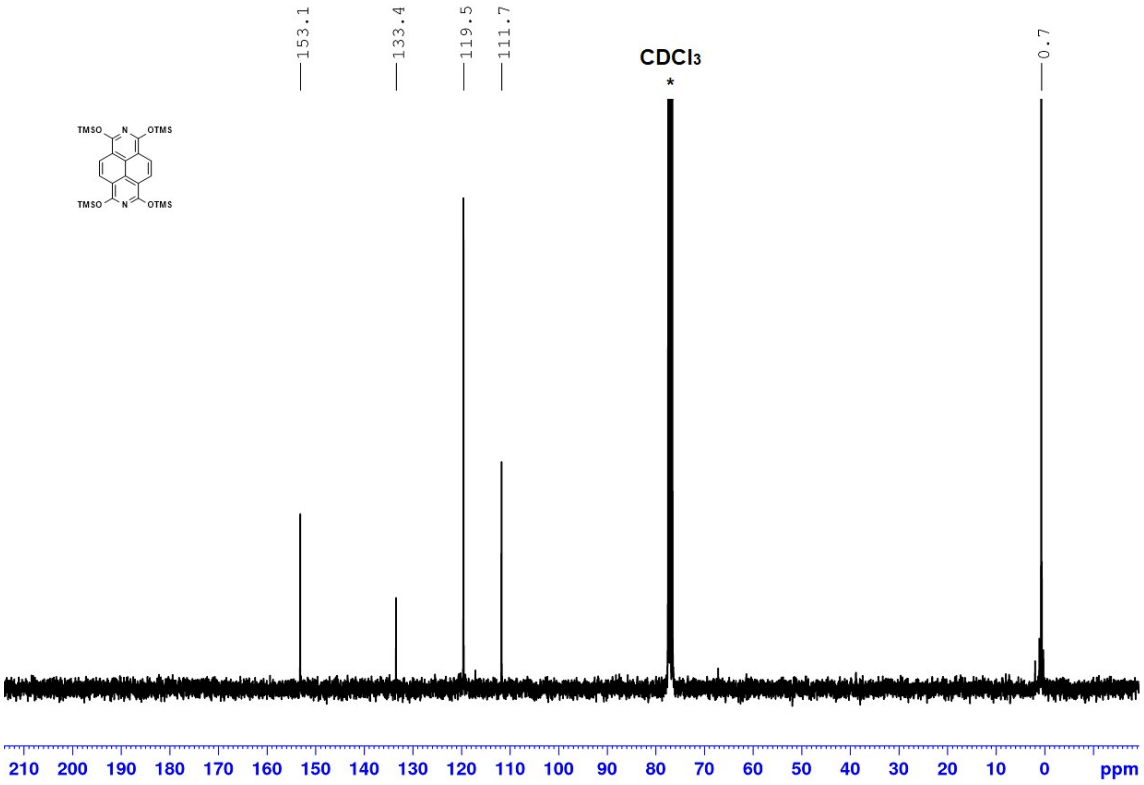


Figure S14. ^{13}C-NMR (75.1 MHz, 298K, $CDCl_3$*) of **2a**.

*1,3,6,8-Tetrakis((triisopropylsilyl)oxy)benzo[lmn][3,8]phenanthroline (**2e**)*

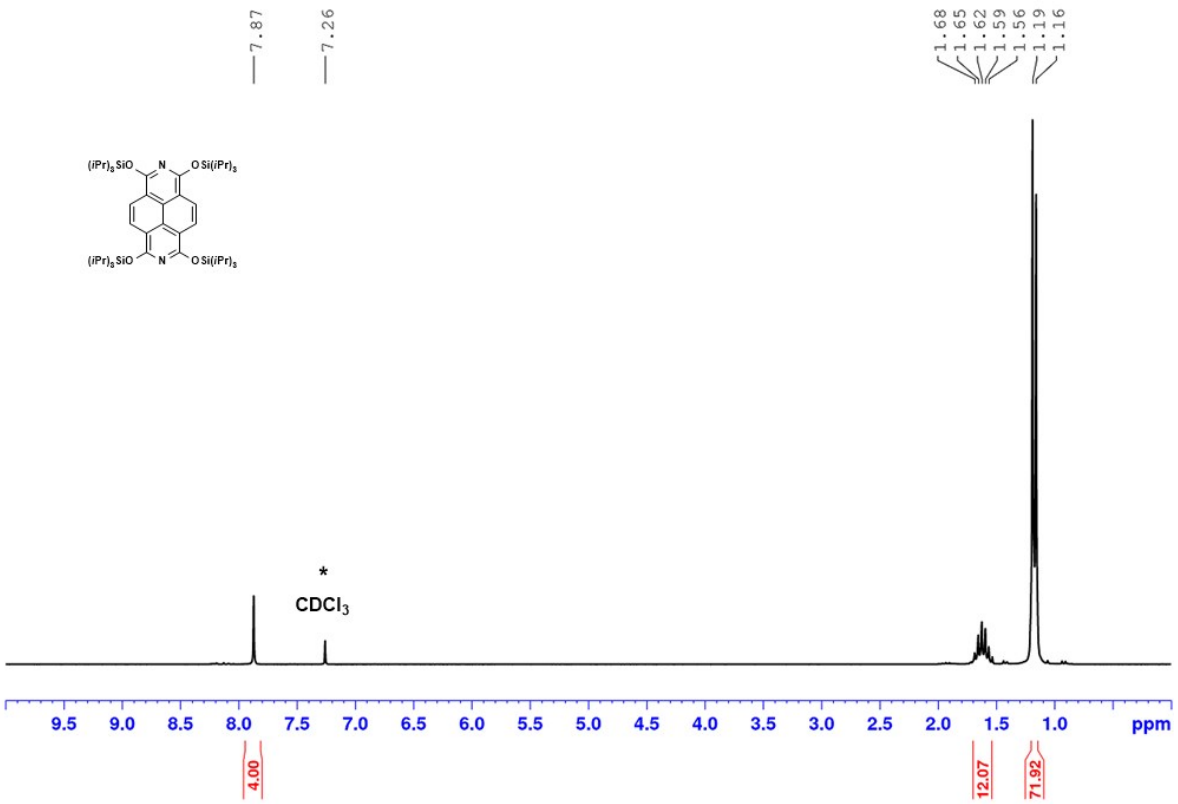


Figure S15. ^{1}H-NMR (300.1 MHz, 298K, $CDCl_3$*) of **2e**.

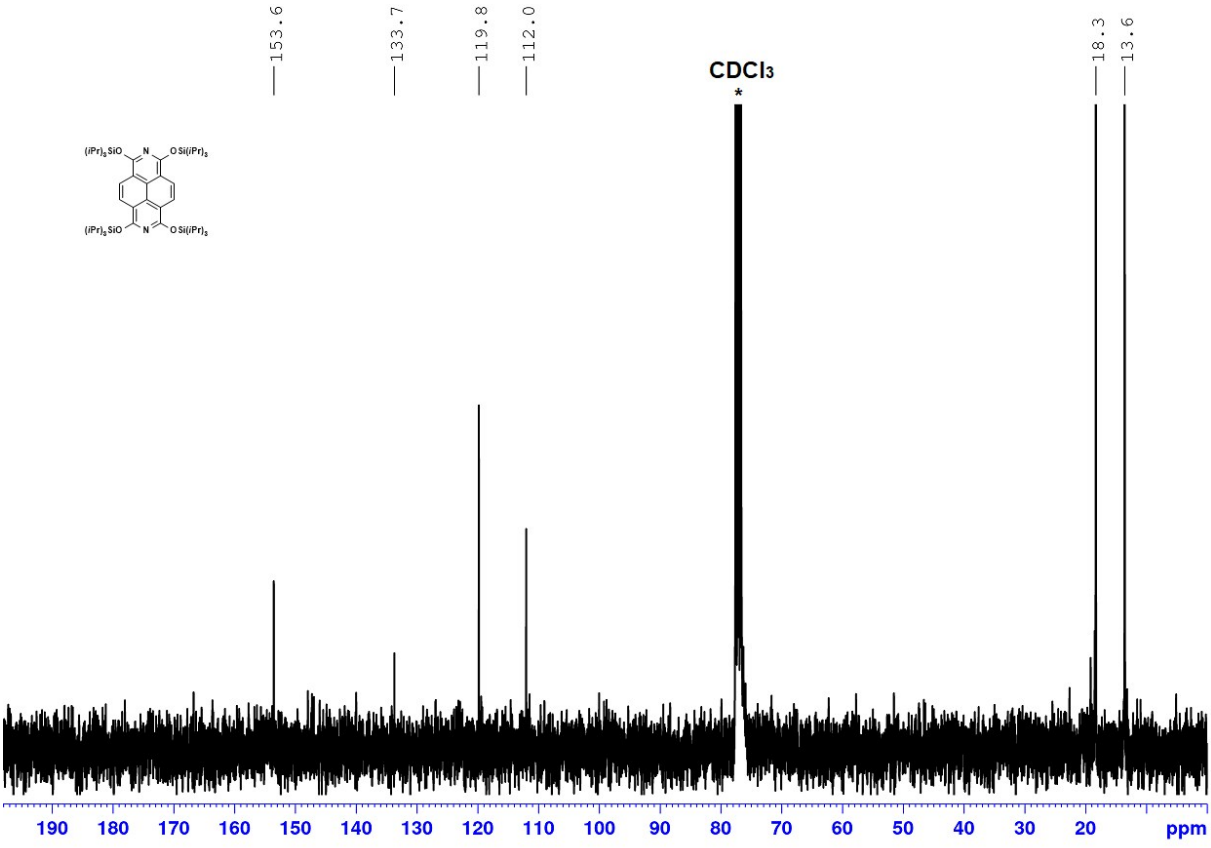


Figure S16. ^{13}C-NMR (75.1 MHz, 298K, $CDCl_3$*) of **2e**.

*1,3,6,8-Tetrakis((tert-butyldimethylsilyl)oxy)benzo[lmn][3,8]phenanthroline (**2f**)*

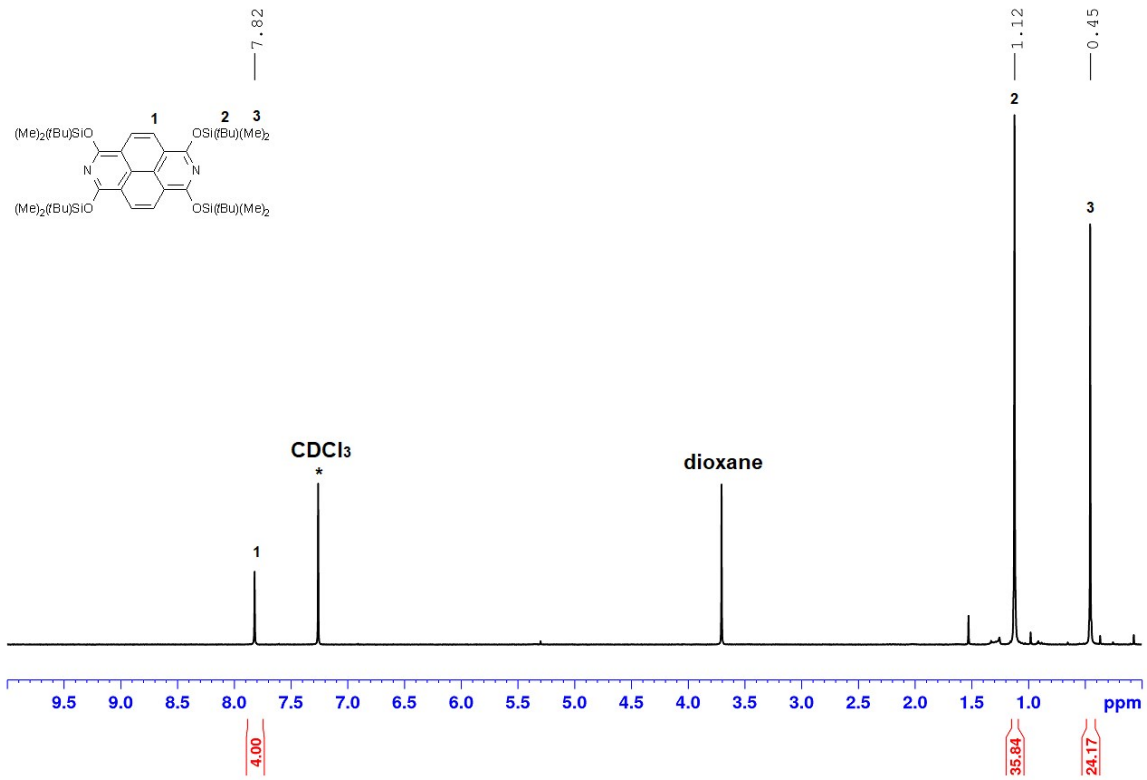


Figure S17. ^{1}H-NMR (300.1 MHz, 298K, $CDCl_3$*) of **2f**. Contains residual 1,4-dioxane.

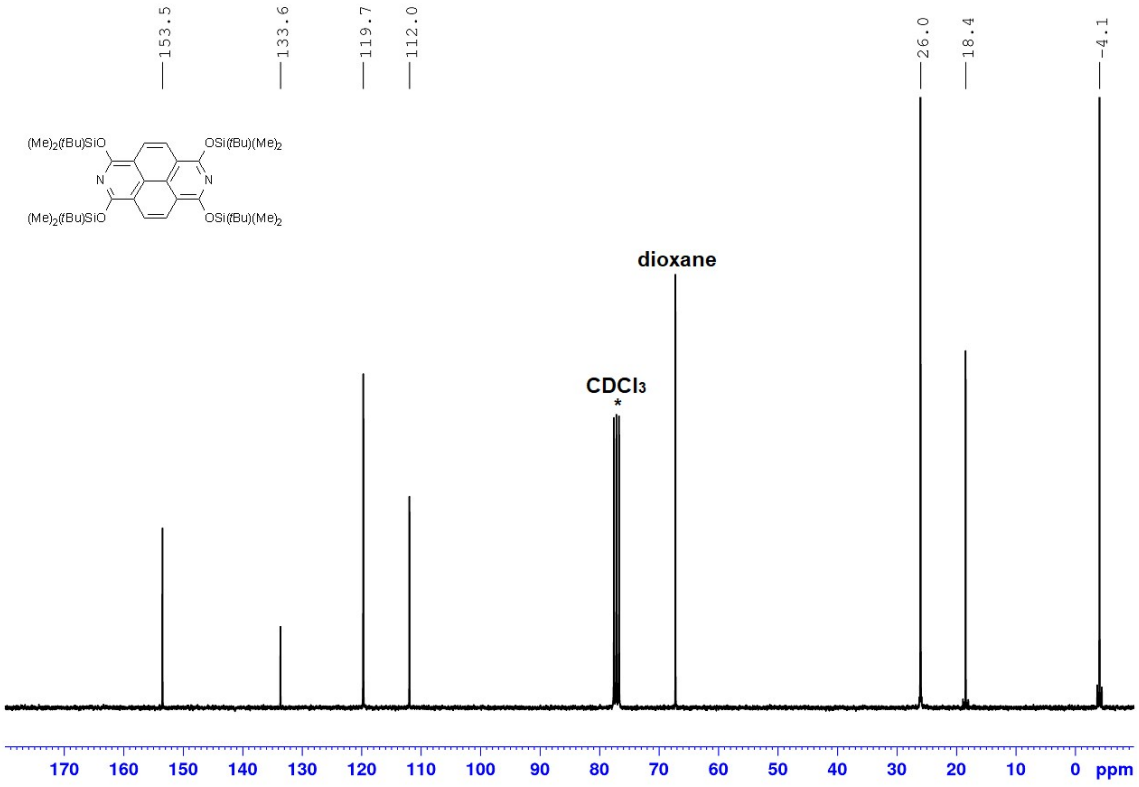


Figure S18. ^{13}C-NMR (75.1 MHz, 298K, $CDCl_3$*) of **2f**. Contains residual 1,4-dioxane.

*Benzo[lmn][3,8]phenanthroline-1,3,6,8-tetrayltetrakis(trifluoromethanesulfonate) (**2d**)*

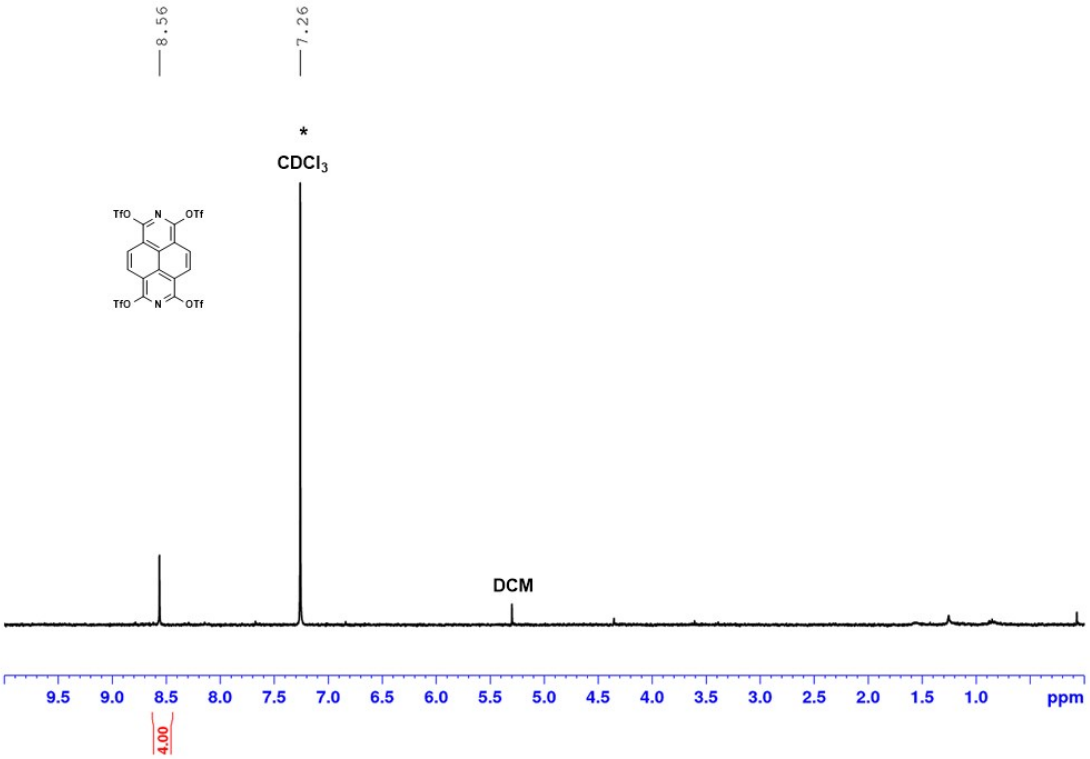


Figure S19. ^{1}H-NMR (300.1 MHz, 298K, $CDCl_3$*) of **2d**. Contains residual dichloromethane.

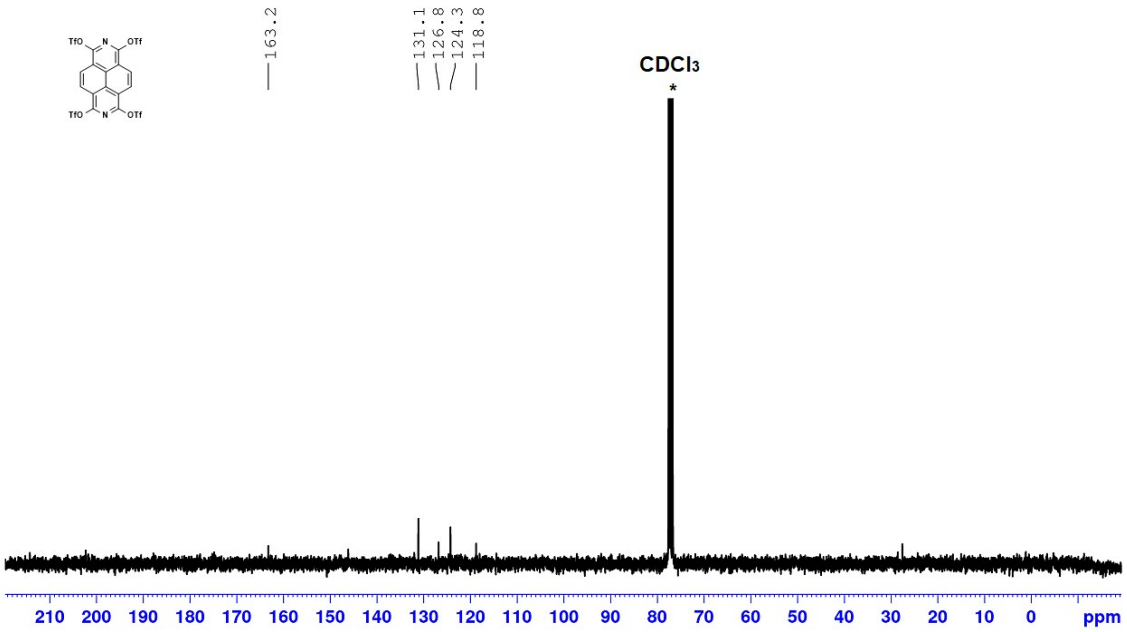


Figure S20. ^{13}C-NMR (75.1 MHz, 298K, $CDCl_3$*) of **2d**.

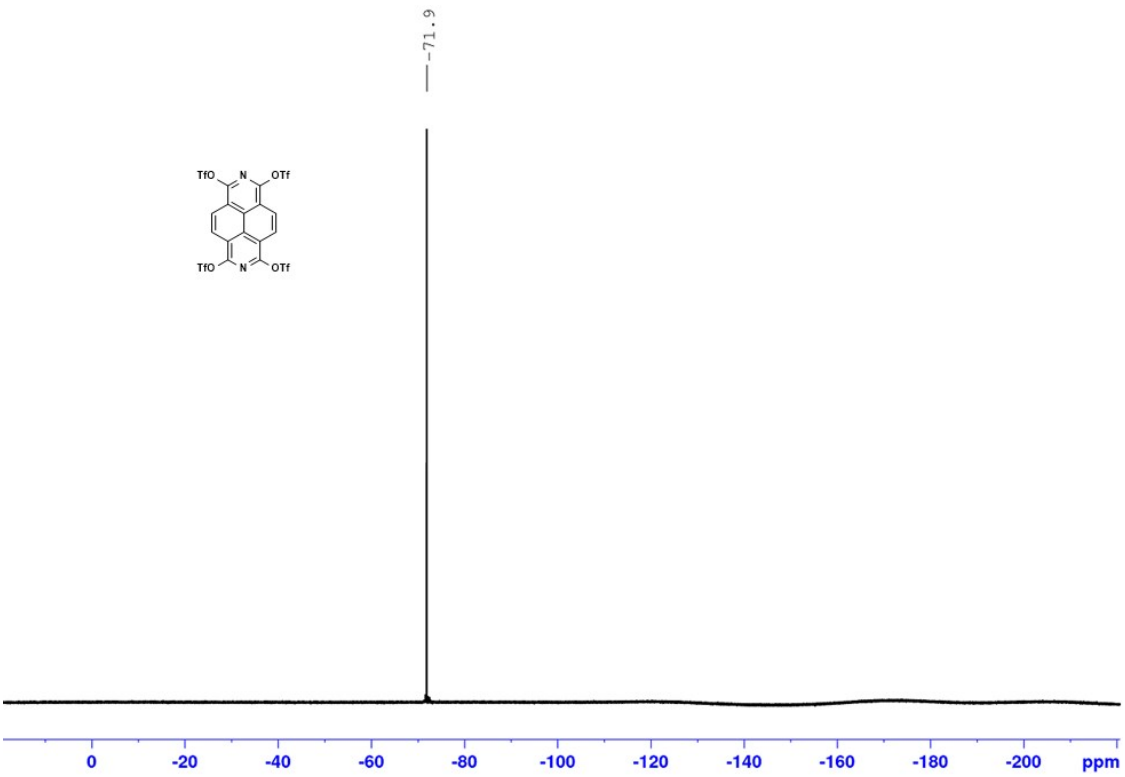


Figure S21. ^{19}F-NMR (235.3 MHz, 298K, $CDCl_3$*) of **2d**.

*1,3,6,8-Tetrakis((trimethylsilyl)ethynyl)benzo[lmn][3,8]phenanthroline (**3b**)*

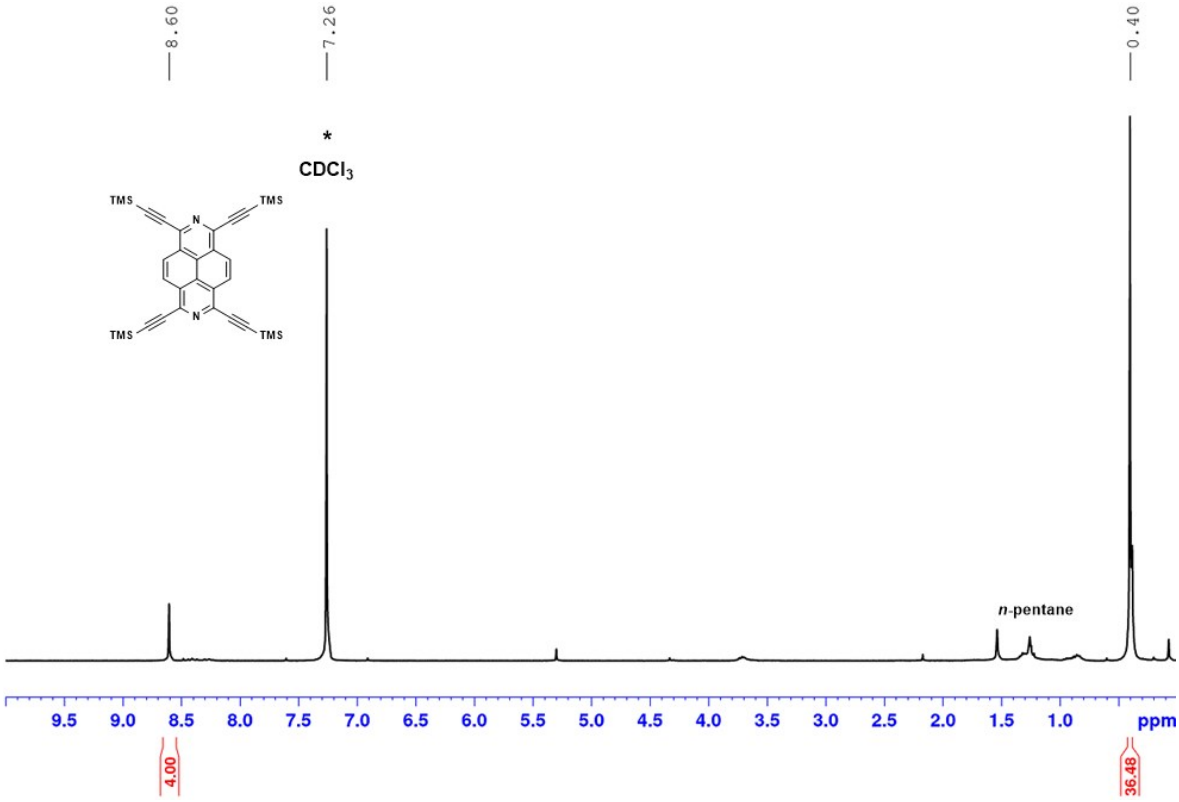


Figure S22. ^{1}H-NMR (300.1 MHz, 298K, $CDCl_3$*) of **3b**. Contains residual *n*-pentane and silicon grease.

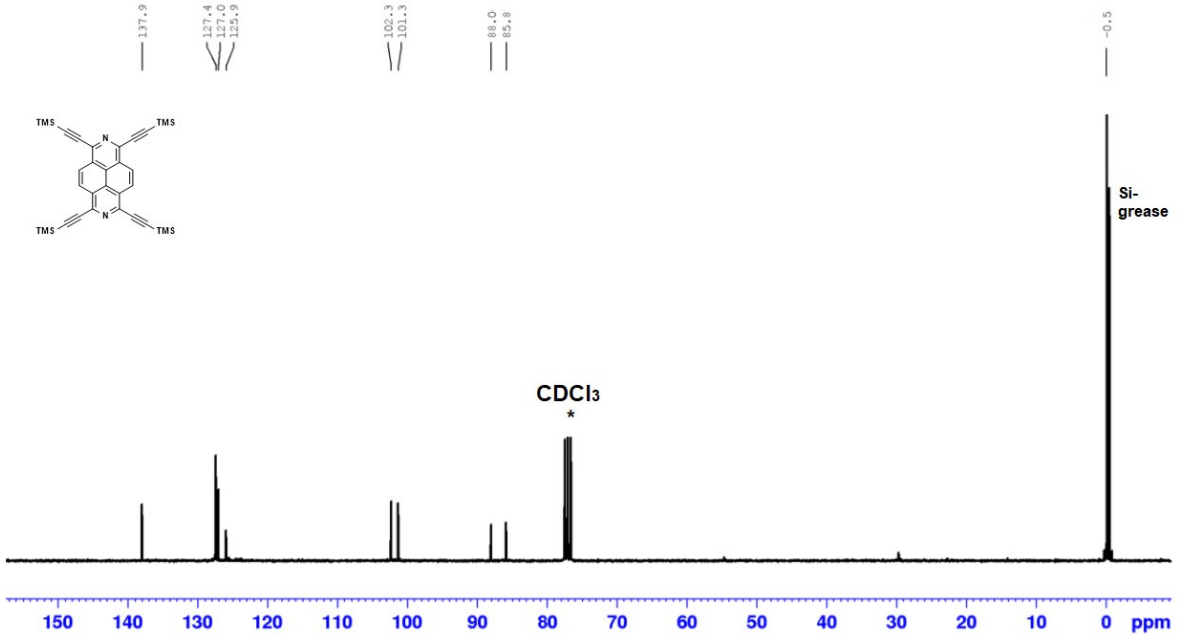


Figure S23. ^{13}C-NMR (75.1 MHz, 298K, $CDCl_3$*) of **3b**.

*1,3,6,8-Tetrakis((4-(tert-butyl)phenyl)ethynyl)benzo[lmn][3,8]phenanthroline (**3d**)*

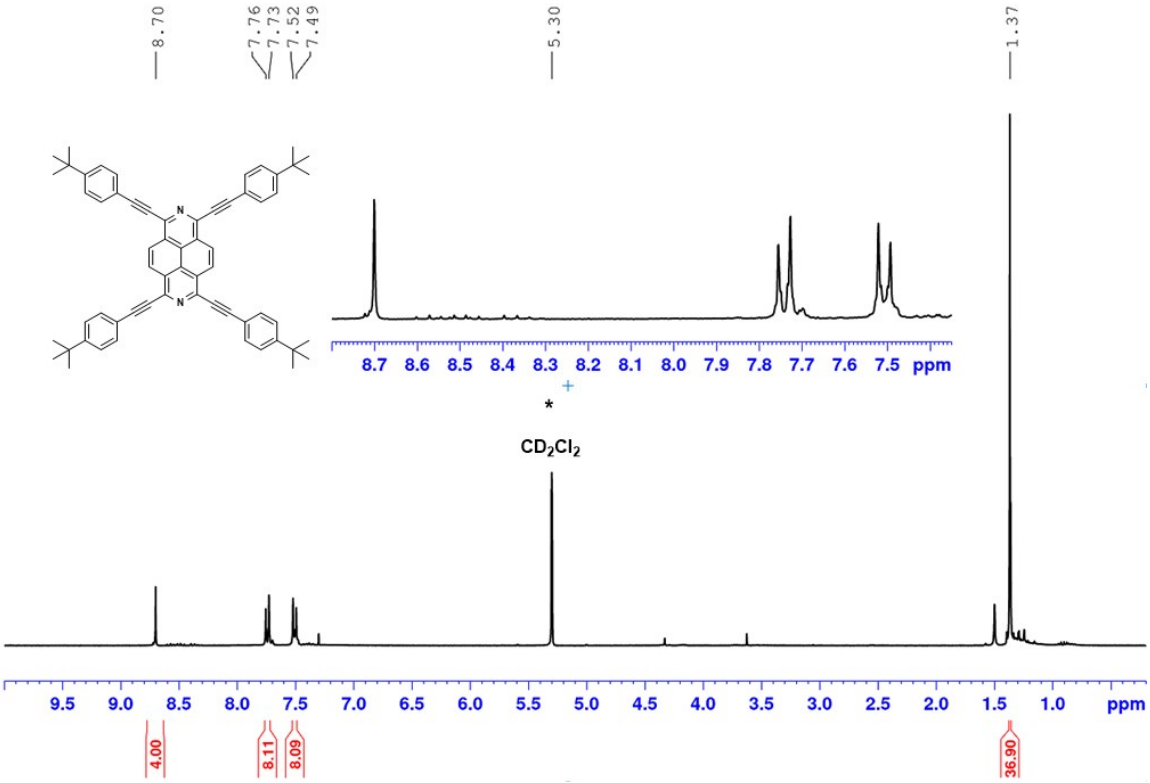


Figure S24. ^{1}H-NMR (300.1 MHz, 298K, CD_2Cl_2*) of **3c**.

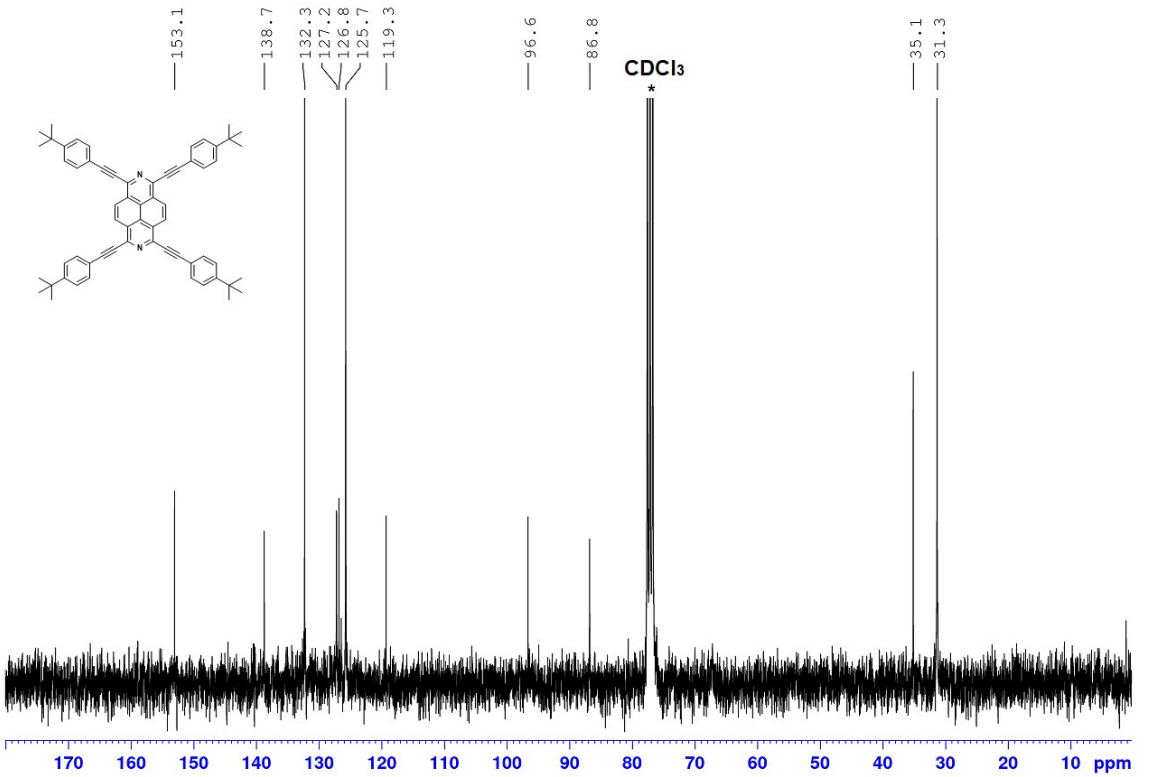


Figure S25. ^{13}C-NMR (75.1 MHz, 298K, $CDCl_3$*) of **3b**.