Supporting information: Benchmarking triplet-triplet annihilation photon upconversion schemes

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S1 Notes on TTET and TTA

Triplet-triplet energy transfer Intermolecular energy transfers are theoretically a combination of Förster resonant energy transfers (FRET) and Dexter-type energy transfers, but in the rapid-diffusion limit, which is a good approximation for all practical purposes of TTA-UC solutions,[1] only the Dexter-type contributes significantly.[2,3] Furthermore, the long-range dipole-dipole energy transfer mechanism underlying FRET depends on the transition moments of the resulting electronic rearrangements, and with multiplicity changes for both the sensitizer and annihilator during TTET (see upper left inset in Fig. 1 of the main text), the FRET mechanism can be neglected. The underlying mechanism of the Dexter theory is an electron exchange relying on electron density overlap, and it, in addition to obeying the Wigner spin conservation rule, thus requires the sensitizer and annihilator to collide or at least be in close proximity (less than 15 Å).[4] The rate of Dexter energy transfer falls off exponentially with intermolecular sensitizer-annihilator distance R_{SA}:[5]

$$k_{\mathrm{Dexter}} \propto J(\lambda) e^{-\frac{2R_{\mathrm{SA}}}{L}} \tag{1}$$

where $J(\lambda)$ is the spectral sensitizer-annihilator overlap integral and L is the effective Bohr-radius describing the spatial extent of their wavefunctions. Experiments at different temperatures have shown that sensitizer-annihilator TTET is more efficient at ambient temperature than at 77 K,[5] proving that TTET has an additional diffusion dependence. The data measured at ambient temperature corresponded very well with the Perrin approximation (within an "active sphere" of radius R_0 related to the effective Bohr-radius L of Eq. (1), the rate of electron transfer is approximated to be infinitely high, while it is set to zero outside), yielding a steady-state TTET rate of:[5]

$$k_{\mathrm{TTET}} = 4\pi D R_0 C_{\mathrm{A}} \tag{2}$$

where C_{A} is the annihilator concentration, D is the overall diffusion coefficient given by the Einstein relation:

$$D = \frac{3k_B T}{6\pi\eta}\left(\frac{1}{R_{\mathrm{S}}} + \frac{1}{R_{\mathrm{A}}}\right) \tag{3}$$

and R_{S} and R_{A} are the effective molecular radii of the sensitizer and annihilator, respectively, while η is the solvent viscosity. Using high relative annihilator concentrations, low viscosity solvents, and small molecular species will thus improve the TTET efficiency,[1] while long-lived sensitizer triplet states are essential too for the triplet exciton diffusion length to be longer than its mean free path.[1,6]

While many parameters of TTET are not trivially modeled sufficiently accurately theoretically, we are, however, able to model the spectral overlap of sensitizers and annihilators fairly simply. Using TD-DFT, we can determine if a sensitizer/annihilator pair is qualitatively and, if reliably benchmarked, quantitatively suitable for TTA-UC by approximating their triplet energies; remember that the lowest sensitizer triplet state should have a slightly higher energy than the lowest annihilator triplet state (see Fig. 1 of the main text).

Triplet-triplet annihilation Similar to TTET, TTA is for all practical purposes a diffusion controlled event governed exclusively by a Dexter mechanism.[1,5,7] While examples of utilizing a mixture of two different annihilators exist in the literature,[8] TTA usually happens between two identical annihilators in the context of TTA-UC as seen in

Fig. 1 of the main text. The possible spin-complexes of two annihilator triplets $^3A^*$ undergoing a diffusion controlled electron exchange (Dexter) mechanism can from a purely spin-statistical view be written as:[7,9]

$$^3A^* + {}^3A^* \rightarrow \begin{cases} {}^5(AA)^* \rightleftharpoons {}^5A^* + {}^1A \\ {}^3(AA)^* \rightleftharpoons {}^3A^* + {}^1A \\ {}^1(AA)^* \rightleftharpoons {}^1A^* + {}^1A \end{cases} \quad (4)$$

with probabilities for direct formation of a quintet, triplet, and singlet complex of 5/9, 3/9, and 1/9, respectively. If accurate, this limits the efficiency of TTA to 11.1 % since the excited singlet state is the only desirable one, and TTA can thus be regarded as the limiting step of TTA-UC. In practice, however, the annihilator triplet resulting from the triplet complex can of course be recycled, while the quintet complex might be dissociative (leading back to the two triplets) or the annihilator quintet $^5A^*$ might decay to a triplet. This leads to theoretical efficiencies of TTA of at least 40 %,[10] and up to 33 % has been reported from experiment.[11] Correcting for the fact that N annihilator triplets produce $N/2$ singlet excited annihilators, the theoretical efficiency is at least 20 %, while the highest experimental value corresponds to 16.5 %. In this study (ref 11), the total quantum yield of TTA-UC was calculated to be 16 %, indicating that TTA is indeed the limiting step.

As with TTET, many relevant properties of TTA is not trivially accessible by calculations. It is though possible to model the requirement of the $^1A^*$ state being at least twice as high in energy as the $^3A^*$ state using *e.g.* TD-DFT with the same challenges and approximations as described in the above paragraphs.

References

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S2 Basis-set investigation

We have tested the basis-set dependence for vertical excitation energies and singlet-triplet energy differences for the ZnP/DPA pair. The test-set includes seven different basis-sets (both Pople style and Dunning's correlation consistent basis-sets) which were used in connection with seven different DFT functionals, namely BLYP, B3LYP, CAM-B3LYP, M06-L, M06, M06-2X, and PBE0 for the vertical excitation energies (see Table S1) and BP86-D3BJ, B3LYP-D3BJ, M06-L, PBE0, ωB97X-D, M06, and M06-2X for the singlet-triplet energy gaps (see Table S2). Our studies illustrate that using a 6-311++(d,p) Pople style basis-set yields energies which are essentially identical to the ones obtained with the smaller 6-31+G(d) basis-set. It is also clearly illustrated that the inclusion of diffuse functions is essential when calculating the energy differences.

Dunning's correlation consistent basis-sets were tested too, but the inclusion of diffuse functions resulted in severe convergence issues. The cc-pVTZ basis-set yielded results which were virtually identical to the ones obtained with the smaller 6-31+G(d) basis-set. The cc-pVDZ basis-set was too small to reproduce the vertical excitations energies obtained with the larger cc-pVTZ and 6-311++G(d,p) basis-sets. However, for singlet-triplet energy gaps, the cc-pVDZ basis-set performed well and yielded similar results as both 6-311++G(d) and cc-pVTZ. Further discussion of the dependence of the calculated quantities on the choice of functional can be found in the main text (Computational Considerations) for the vertical excitation energies and in e.g. *J. Comput. Chem., vol. 25, pp. 1463-1473, 2004* or *Phys. Chem. Chem. Phys., vol. 10, pp. 6615-6620, 2008* for the effects of including dispersion correction in the functionals (relevant for BP86-D3BJ, B3LYP-D3BJ, and ωB97X-D) for geometry optimizations.

Method	6-31+G(d)	6-311G	6-311G(d)	6-311+G(d)	6-311++G(d,p)	cc-pVDZ	cc-pVTZ	cc-pVQZ
# basis func.	529	387	514	622	670	439	956	1784
BLYP	2.34	2.36	2.32	2.34	2.33	2.36	2.34	2.33
B3LYP	2.46	2.48	2.44	2.46	2.45	2.48	2.45	*
CAM-B3LYP	2.41	2.45	2.38	2.40	2.39	2.43	2.39	2.38
M06-L	2.42	2.44	2.40	2.41	2.41	2.44	2.40	2.40
M06	2.40	2.44	2.38	2.39	2.38	2.41	2.38	2.37
M06-2X	2.50	2.53	2.46	2.48	2.47	2.51	2.47	2.46
PBE0	2.50	2.53	2.47	2.49	2.48	2.51	2.48	2.47

* Indicates that the optimization did not converge.

Table S1: Vertical TD-DFT excitation energies in eV for ZnP optimized in a vacuum using different functionals and basis-sets.

Method	6-31+G(d)	6-311G	6-311G(d,p)	6-311+G(d)	6-311++G(d,p)	cc-pVDZ	cc-pVTZ
				ZnP			
# basis func.	529	387	550	622	670	439	956
BP86-D3BJ	1.54	1.52	1.52	1.54	1.54	1.54	1.54
B3LYP-D3BJ	1.54	1.52	1.51	1.58	1.58	1.59	1.54
M06-L	1.56	1.52	1.53	1.56	1.56	1.57	1.57
PBE0	1.54	1.50	1.50	1.54	1.54	1.54	1.54
ωB97X-D	1.41	1.37	1.38	1.44	1.44	1.44	1.46
M06	1.52	1.49	1.51	1.54	1.55	1.52	1.58
M06-2X	1.63	1.57	1.59	1.63	1.63	1.66	1.65
				DPA			
# basis func.	530	392	576	626	698	454	1032
BP86-D3BJ	1.55	1.62	1.58	1.57	1.57	1.57	1.58
B3LYP-D3BJ	1.66	1.70	1.66	1.67	1.65	1.65	1.67
M06-L	1.57	1.58	1.53	1.54	1.54	1.54	1.52
PBE0	1.63	1.66	1.61	1.61	1.61	1.60	1.62
ωB97X-D	1.69	1.75	1.70	1.69	1.69	1.66	1.75
M06	1.56	1.63	1.59	1.60	*	1.53	1.57
M06-2X	1.81	*	1.84	1.79	1.84	1.88	1.83

* Indicates that the optimization did not converge.

Table S2: Energy difference in eV between the optimized ground state (S_0) and the optimized first excited triplet state (T_1) of ZnP and DPA using different functionals and basis-sets.

S3 Geometries

In this section, atom coordinate files and structures for all systems are presented. All atom coordinate files (with values in Angstrom) and figures are of the respective optimized ground state (S_0) structures using the solvent and level of theory stated in the figure captions.

S3.1 Biacetyl

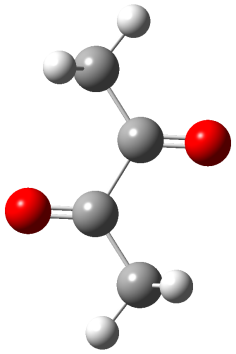

Figure S1: M06-2X/6-311+G(d) optimized ground state geometry of biacetyl in benzene modelled by IEFPCM.

	X	Y	Z
C	0.4053810	0.6609330	-0.0002050
O	1.6085690	0.6067210	-0.0011550
C	-0.4053810	-0.6609330	0.0002050
O	-1.6085690	-0.6067210	0.0011550
C	-0.3913320	1.9313680	0.0003760
H	-1.0452820	1.9602820	-0.8740590
H	-1.0437430	1.9603700	0.8759650
H	0.2798140	2.7873080	-0.0002410
C	0.3913320	-1.9313680	-0.0003760
H	1.0437430	-1.9603700	-0.8759650
H	1.0452820	-1.9602820	0.8740590
H	-0.2798140	-2.7873080	0.0002410

S3.2 ZnP

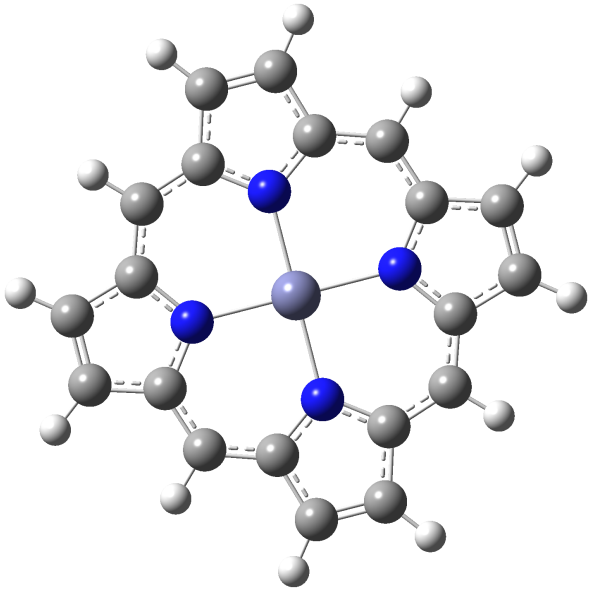

Figure S2: M06-L/6-311+G(d) optimized ground state geometry of ZnP in PhCl modelled by IEFPCM.

	X	Y	Z
C	1.7118970	-3.9433990	-0.0000060
H	2.5710410	-4.6050960	-0.0000060
C	1.7766950	-2.5050600	-0.0000060
C	2.9475780	-1.7462020	-0.0000070
H	3.8839440	-2.3008630	-0.0000040
C	3.0505830	-0.3546240	-0.0000050
C	4.2806740	0.3921320	0.0000190
H	5.2738430	-0.0436430	0.0000350
C	3.9434240	1.7119440	-0.0000200
H	4.6051460	2.5710690	-0.0000340
C	2.5050910	1.7767760	0.0000000
C	1.7462030	2.9476390	0.0000010
H	2.3008200	3.8840320	0.0000020
C	0.3546210	3.0505800	0.0000010
C	-0.3921310	4.2806800	0.0000290
H	0.0436570	5.2738430	0.0000490
C	-1.7119360	3.9434290	-0.0000240
H	-2.5710740	4.6051340	-0.0000460
C	-1.7767520	2.5050850	0.0000050
C	-2.9476660	1.7462680	0.0000050
H	-3.8840200	2.3009500	-0.0000020
C	-3.0506570	0.3546950	0.0000040
C	-4.2807250	-0.3921020	-0.0000010
H	-5.2739030	0.0436500	-0.0000040
C	-3.9434210	-1.7118930	0.0000050
H	-4.6050980	-2.5710530	0.0000060
C	-2.5050700	-1.7766590	0.0000010
C	-1.7462630	-2.9475810	-0.0000020
H	-2.3009730	-3.8839180	-0.0000020
C	-0.3546930	-3.0506250	-0.0000030
C	0.3920960	-4.2806890	-0.0000070
H	-0.0436530	-5.2738680	-0.0000080
N	1.9877590	0.5087790	-0.0000010
N	0.5086690	-1.9877730	-0.0000020
N	-1.9877870	-0.5086390	0.0000030
N	-0.5087650	1.9877410	0.0000040
Zn	0.0001280	-0.0001120	0.0000010

S3.3 ZnOEP

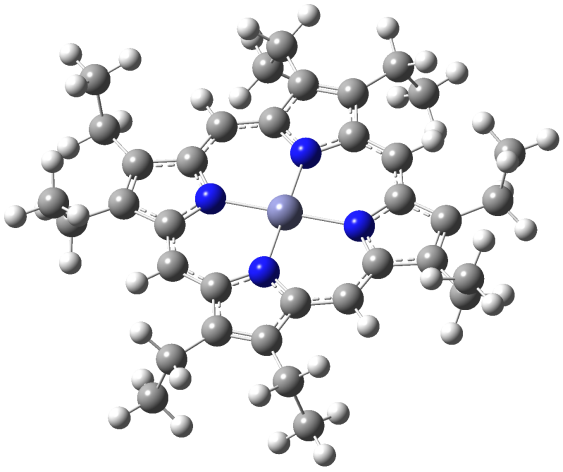

Figure S3: M06-L/6-311+G(d) optimized ground state geometry of ZnOEP in PhCl modelled by IEFPCM.

	X	Y	Z
C	-3.9479180	1.7287600	-0.0043210
C	-2.5021290	1.7806820	-0.0057800
C	-1.7360660	2.9466230	-0.0141080
H	-2.2883760	3.8849900	-0.0201250
C	-0.3447630	3.0514000	-0.0114930
C	0.4009460	4.2908580	-0.0094010
C	1.7287890	3.9479370	0.0040810
C	1.7806720	2.5021600	0.0054770
C	2.9466040	1.7361150	0.0140640
H	3.8849690	2.2884360	0.0203210
C	3.0514000	0.3448150	0.0115600
C	4.2908680	-0.4008810	0.0098090
C	3.9479610	-1.7287300	-0.0036700
C	2.5021800	-1.7806300	-0.0054080
C	1.7361270	-2.9465650	-0.0139800
H	2.2884430	-3.8849310	-0.0199980
C	0.3448240	-3.0513480	-0.0116490
C	-0.4008830	-4.2908120	-0.0098380
C	-1.7287270	-3.9478960	0.0034500
C	-1.7806170	-2.5021180	0.0050180
C	-2.9465520	-1.7360820	0.0135140
H	-3.8849180	-2.2884070	0.0196080
C	-3.0513500	-0.3447800	0.0110740
C	-4.2908180	0.4009060	0.0092340
N	0.5132890	1.9853700	-0.0022930
N	-1.9853360	0.5132980	0.0017850
N	-0.5132370	-1.9853220	-0.0024600
N	1.9853830	-0.5132540	0.0021370
Zn	0.0000180	0.0000210	-0.0002820
C	-4.8513710	2.9162000	0.0239890
C	-5.0353610	3.4968900	1.4239220
H	-5.8313620	2.6430730	-0.3863040
H	-4.4653580	3.6977890	-0.6440630
H	-5.6938480	4.3706200	1.4125410
H	-5.4728850	2.7606590	2.1051540
H	-4.0797970	3.8080350	1.8582370
C	-5.6554820	-0.2001350	0.0631010
C	-6.0511320	-0.6621270	1.4636100
H	-5.7206130	-1.0503780	-0.6293330
H	-6.3920750	0.5268260	-0.3004580
H	-7.0518470	-1.1044960	1.4721580
H	-5.3540100	-1.4122560	1.8505400
H	-6.0505260	0.1716230	2.1723640
C	-2.9162490	-4.8512290	-0.0247320
C	-3.4986580	-5.0333730	-1.4241850
H	-3.6970460	-4.4659780	0.6446930
H	-2.6427270	-5.8317530	0.3840240
H	-4.3724620	-5.6917560	-1.4125450
H	-3.8102180	-4.0772190	-1.8569130
H	-2.7633440	-5.4701240	-2.1068960
C	0.2002220	-5.6554720	-0.0630610
C	0.6627400	-6.0517400	-1.4632040
H	-0.5267780	-6.3919590	0.3006330
H	1.0502640	-5.7202320	0.6296500
H	1.1053290	-7.0523640	-1.4710440
H	-0.1707230	-6.0517180	-2.1722920
H	1.4128810	-5.3546740	-1.8502210
C	4.8513200	-2.9162370	0.0245910
C	5.0338690	-3.4982260	1.4241690
H	5.8317310	-2.6428150	-0.3844980
H	4.4659090	-3.6972260	-0.6445170
H	5.6923030	-4.3719950	1.4126150
H	5.4707620	-2.7626810	2.1065410
H	4.0778530	-3.8097180	1.8572470
C	5.6555180	0.2002090	0.0634200
C	6.0514550	0.6624470	1.4637500
H	5.7204600	1.0503690	-0.6291310
H	6.3920800	-0.5267460	-0.3002140
H	7.0520910	1.1050000	1.4719300
H	5.3543160	1.4125230	1.8507660
H	6.0512270	-0.1711740	2.1726550
C	2.9163220	4.8512690	-0.0237690
C	3.4989150	5.0336920	-1.4231080
H	3.6970280	4.4658770	0.6456810
H	2.6427550	5.8317120	0.3851480
H	4.3727020	5.6920940	-1.4112230
H	3.8105590	4.0776280	-1.8559760
H	2.7636850	5.4705560	-2.1058370
C	-0.2001410	5.6555260	-0.0626040
C	-0.6624650	6.0518950	-1.4627810
H	0.5268170	6.3919770	0.3012450
H	-1.0502800	5.7202440	0.6299910
H	-1.1050790	7.0525070	-1.4706070
H	0.1710980	6.0519480	-2.1717530
H	-1.4125330	5.3548380	-1.8499570

S3.4 PdP

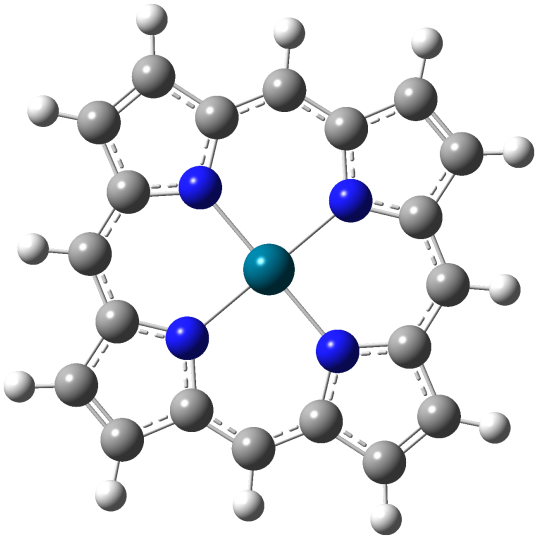

Figure S4: M06-L/6-311+G(d)/aug-cc-pVTZ-PP optimized ground state geometry of PdP in PhCl modelled by IEFPCM.

	X	Y	Z
C	2.7955730	3.2391180	-0.0004920
H	3.0118360	4.3012130	-0.0007040
C	1.4732060	2.6778900	-0.0001490
C	0.2943870	3.4093130	-0.0000610
H	0.3878720	4.4927270	-0.0001670
C	-0.9925610	2.8907520	0.0000380
C	-2.1990250	3.6705270	0.0000970
H	-2.2301120	4.7539890	0.0000810
C	-3.2391540	2.7954600	0.0000310
H	-4.3012220	3.0118220	-0.0000390
C	-2.6779420	1.4732400	0.0000200
C	-3.4093230	0.2943450	-0.0001030
H	-4.4927330	0.3878590	-0.0001740
C	-2.8907250	-0.9924830	-0.0001780
C	-3.6705600	-2.1990460	-0.0002850
H	-4.7540330	-2.2299870	-0.0003260
C	-2.7955700	-3.2391200	-0.0004890
H	-3.0118330	-4.3012150	-0.0007010
C	-1.4732030	-2.6778910	-0.0001470
C	-0.2943870	-3.4093150	-0.0000610
H	-0.3878720	-4.4927280	-0.0001670
C	0.9925580	-2.8907540	0.0000380
C	2.1990220	-3.6705280	0.0000960
H	2.2301080	-4.7539900	0.0000800
C	3.2391500	-2.7954620	0.0000290
H	4.3012180	-3.0118240	-0.0000410
C	2.6779390	-1.4732420	0.0000180
C	3.4093230	-0.2943480	-0.0001050
H	4.4927320	-0.3878640	-0.0001770
C	2.8907280	0.9924810	-0.0001810
C	3.6705640	2.1990430	-0.0002880
H	4.7540360	2.2299840	-0.0003300
N	-1.3091920	1.5564170	0.0001580
N	1.5564220	1.3091520	-0.0001040
N	1.3091880	-1.5564180	0.0001570
N	-1.5564170	-1.3091530	-0.0001020
Pd	0.0000000	0.0000030	0.0003250

S3.5 PdOEP

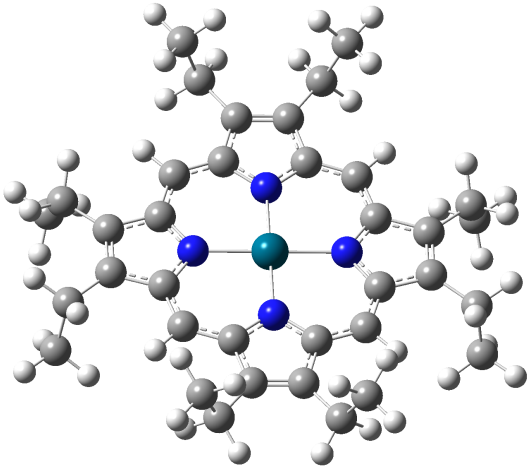

Figure S5: M06-L/6-311+G(d)/aug-cc-pVTZ-PP optimized ground state geometry of PdOEP in a vacuum.

	X	Y	Z
C	-4.2408440	-0.6389240	-0.0396210
C	-2.8618280	-1.0673890	-0.0187350
C	-2.4392250	-2.3882390	-0.0046050
H	-3.2165560	-3.1495010	-0.0077900
C	-1.1278320	-2.8383000	0.0144790
C	-0.7282930	-4.2267490	0.0378290
C	0.6389260	-4.2409850	0.0405970
C	1.0673700	-2.8619650	0.0190340
C	2.3882120	-2.4393630	0.0046140
H	3.1494570	-3.2167000	0.0081570
C	2.8382720	-1.1279830	-0.0149580
C	4.2267410	-0.7284610	-0.0382210
C	4.2409820	0.6387630	-0.0411590
C	2.8619530	1.0672090	-0.0197210
C	2.4393560	2.3880480	-0.0051900
H	3.2166740	3.1493190	-0.0082750
C	1.1279760	2.8381020	0.0142510
C	0.7284620	4.2265540	0.0376040
C	-0.6387490	4.2408100	0.0404470
C	-1.0672190	2.8618020	0.0190660
C	-2.3880680	2.4392140	0.0050360
H	-3.1493140	3.2165530	0.0086970
C	-2.8381410	1.1278310	-0.0142010
C	-4.2265980	0.7282870	-0.0369750
N	-0.0215520	-2.0332940	0.0047770
N	-2.0331430	0.0215350	-0.0048940
N	0.0216900	2.0331030	0.0047030
N	2.0332650	-0.0217020	-0.0055340
C	-5.4151820	-1.5564450	-0.1066040
C	-5.6665200	-2.1053390	-1.5086350
H	-6.3112420	-1.0307340	0.2454220
H	-5.2793410	-2.3931890	0.5924540
H	-6.5236600	-2.7852590	-1.5288730
H	-5.8658160	-1.2990590	-2.2211960
H	-4.7975460	-2.6541380	-1.8854660
C	-5.3803330	1.6717520	-0.1026250
C	-5.6058290	2.2476990	-1.4983940
H	-5.2354600	2.4947450	0.6110530
H	-6.2914460	1.1599090	0.2312590
H	-6.4451660	2.9496300	-1.5145250
H	-4.7207330	2.7798700	-1.8611640
H	-5.8203610	1.4578110	-2.2246590
C	-1.5563740	5.4150540	0.1078320
C	-2.1068820	5.6648130	1.5095130
H	-2.3923820	5.2798980	-0.5922440
H	-1.0303580	6.3115310	-0.2426890
H	-2.7868490	6.5219130	1.5299100
H	-2.6561150	4.7954280	1.8847510
H	-1.3014810	5.8633350	2.2232610
C	1.6720230	5.3802040	0.1033640
C	2.2489390	5.6048750	1.4988570
H	1.1601150	6.2915380	-0.2298350
H	2.4946040	5.2355690	-0.6108330
H	2.9511690	6.4439640	1.5148780
H	1.4596710	5.8193420	2.2258070
H	2.7810830	4.7194160	1.8608010
C	5.4151480	1.5565280	-0.1082270
C	5.6637030	2.1094630	-1.5091800
H	6.3119460	1.0299610	0.2406210
H	5.2806110	2.3913960	0.5933460
H	6.5207540	2.7895060	-1.5290470
H	5.8617110	1.3053820	-2.2245320
H	4.7940300	2.6593270	-1.8828050
C	5.3803170	-1.6721840	-0.1033540
C	5.6054950	-2.2496660	-1.4985400
H	5.2352700	-2.4945010	0.6110640
H	6.2915920	-1.1603260	0.2300650
H	6.4444110	-2.9521170	-1.5138870
H	4.7200890	-2.7817310	-1.8607220
H	5.8205320	-1.4607720	-2.2257110
C	1.5566280	-5.4151770	0.1079180
C	2.1082330	-5.6642620	1.5092910
H	2.3921180	-5.2803310	-0.5928440
H	1.0303810	-6.3118350	-0.2417840
H	2.7882360	-6.5213370	1.5295370
H	2.6577510	-4.7947070	1.8837090
H	1.3034250	-5.8624790	2.2237820
C	-1.6718840	-5.3803810	0.1036070
C	-2.2489030	-5.6050280	1.4990640
H	-1.1599980	-6.2917320	-0.2295720
H	-2.4944280	-5.2357290	-0.6106270
H	-2.9511840	-6.4440760	1.5150210
H	-1.4597220	-5.8195510	2.2260850
H	-2.7810290	-4.7195440	1.8609720
Pd	0.0000560	-0.0000980	-0.0005580

S3.6 PtP

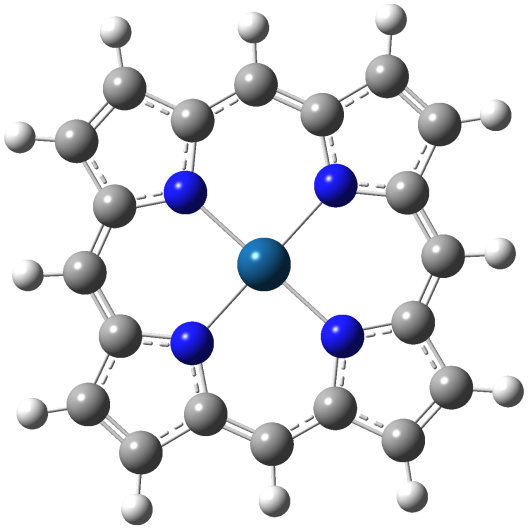

Figure S6: M06-L/6-311+G(d)/aug-cc-pVTZ-PP optimized ground state geometry of PtP in PhCl modelled by IEFPCM.

	X	Y	Z
C	3.0710580	-2.9769390	-0.0001820
H	3.3801370	-4.0155590	-0.0003600
C	1.7044270	-2.5374470	0.0000850
C	0.5956560	-3.3691260	0.0000800
H	0.7853450	-4.4398880	0.0000180
C	-0.7306180	-2.9681640	-0.0000300
C	-1.8634390	-3.8494660	-0.0000350
H	-1.7978070	-4.9313600	0.0000560
C	-2.9769460	-3.0710590	-0.0003650
H	-4.0154300	-3.3806520	-0.0005420
C	-2.5375790	-1.7043110	0.0000380
C	-3.3692290	-0.5956010	0.0001490
H	-4.4400280	-0.7850730	0.0001380
C	-2.9682130	0.7307170	0.0001010
C	-3.8495280	1.8634250	0.0002380
H	-4.9313850	1.7973090	0.0004010
C	-3.0710470	2.9769460	-0.0001870
H	-3.3801240	4.0155680	-0.0003710
C	-1.7044190	2.5374480	0.0000860
C	-0.5956550	3.3691230	0.0000790
H	-0.7853440	4.4398860	0.0000180
C	0.7306100	2.9681620	-0.0000320
C	1.8634260	3.8494700	-0.0000250
H	1.7977920	4.9313640	0.0000750
C	2.9769340	3.0710680	-0.0003810
H	4.0154160	3.3806660	-0.0005710
C	2.5375710	1.7043180	0.0000390
C	3.3692280	0.5956100	0.0001490
H	4.4400260	0.7850840	0.0001320
C	2.9682180	-0.7307080	0.0001000
C	3.8495370	-1.8634130	0.0002260
H	4.9313940	-1.7972920	0.0003810
N	-1.1634960	-1.6636290	-0.0001220
N	1.6636930	-1.1634330	-0.0000030
N	1.1634880	1.6636270	-0.0001220
N	-1.6636840	1.1634330	-0.0000020
Pt	0.0000010	-0.0000050	0.0000200

S3.7 PtOEP

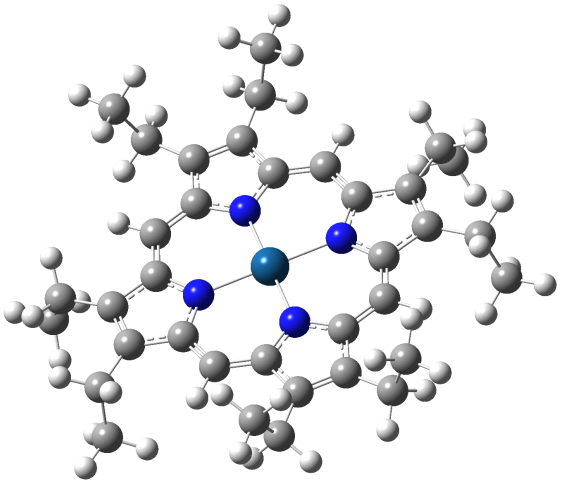

Figure S7: M06-L/6-311+G(d)/aug-cc-pVTZ-PP optimized ground state geometry of PtOEP in PhCl modelled by IEFPCM.

	X	Y	Z
C	-1.4214980	4.0470690	0.0043680
C	-0.3955790	3.0313400	0.0023470
C	0.9685770	3.2745690	-0.0032320
H	1.2778850	4.3175130	-0.0040070
C	1.9807460	2.3278950	-0.0066790
C	3.3935960	2.6229680	-0.0075150
C	4.0471020	1.4214850	-0.0040860
C	3.0313550	0.3955590	-0.0023690
C	3.2745660	-0.9686180	0.0032150
H	4.3175070	-1.2779310	0.0042010
C	2.3278400	-1.9807810	0.0066630
C	2.6228610	-3.3936200	0.0078180
C	1.4214530	-4.0470500	0.0043560
C	0.3955630	-3.0313070	0.0023710
C	-0.9685670	-3.2745240	-0.0031700
H	-1.2778550	-4.3174750	-0.0038720
C	-1.9807130	-2.3278580	-0.0066570
C	-3.3935430	-2.6229210	-0.0075590
C	-4.0470100	-1.4215270	-0.0041610
C	-3.0312900	-0.3955970	-0.0023880
C	-3.2745310	0.9685830	0.0032590
H	-4.3174800	1.2778620	0.0041980
C	-2.3278280	1.9807760	0.0067780
C	-2.6228870	3.3936100	0.0079040
N	1.7842000	0.9692320	-0.0026950
N	-0.9692100	1.7842060	0.0025130
N	-1.7841540	-0.9692310	-0.0026740
N	0.9692170	-1.7841840	0.0024540
C	-1.1626070	5.5157590	0.0452620
C	-0.8338570	6.0279030	1.4452850
H	-2.0382140	6.0514400	-0.3410430
H	-0.3420690	5.7727670	-0.6382270
H	-0.6374350	7.1042700	1.4425520
H	-1.6592050	5.8428680	2.1395760
H	0.0499170	5.5311620	1.8584120
C	-3.9958290	3.9752690	0.0571010
C	-4.6111430	3.9440230	1.4539930
H	-4.6557190	3.4445220	-0.6425620
H	-3.9654380	5.0105600	-0.3032280
H	-5.6190930	4.3696400	1.4571090
H	-4.6824680	2.9220670	1.8398920
H	-4.0078100	4.5142890	2.1670510
C	-5.5156950	-1.1626290	-0.0450300
C	-6.0276140	-0.8330060	-1.4449400
H	-5.7728130	-0.3424950	0.6389130
H	-6.0514070	-2.0384850	0.3406740
H	-7.1039890	-0.6366320	-1.4422740
H	-5.5308350	0.0510820	-1.8573700
H	-5.8424030	-1.6578740	-2.1397730
C	-3.9752450	-3.9958540	-0.0564110
C	-3.9447890	-4.6111000	-1.4533500
H	-5.0103140	-3.9654420	0.3045460
H	-3.4441010	-4.6557700	0.6429180
H	-4.3704310	-5.6190410	-1.4563090
H	-4.5154090	-4.0077030	-2.1660760
H	-2.9230180	-4.6824180	-1.8397520
C	1.1625330	-5.5157280	0.0453750
C	0.8333780	-6.0275950	1.4454130
H	2.0382390	-6.0514820	-0.3406160
H	0.3421570	-5.7728400	-0.6382720
H	0.6369870	-7.1039680	1.4428520
H	1.6584930	-5.8423760	2.1399380
H	-0.0505570	-5.5307870	1.8581320
C	3.9957750	-3.9753510	0.0569620
C	4.6108630	-3.9446040	1.4539690
H	4.6557860	-3.4443640	-0.6423980
H	3.9653900	-5.0104990	-0.3037750
H	5.6187820	-4.3702980	1.4571470
H	4.6821900	-2.9227520	1.8401450
H	4.0073550	-4.5150230	2.1667570
C	5.5157930	1.1625640	-0.0448760
C	6.0278080	0.8330820	-1.4447820
H	5.7728480	0.3423530	0.6389980
H	6.0514900	2.0383710	0.3409590
H	7.1041800	0.6366910	-1.4420610
H	5.5310430	-0.0509540	-1.8573400
H	5.8426600	1.6580280	-2.1395390
C	3.9753020	3.9959090	-0.0563140
C	3.9450150	4.6111410	-1.4532640
H	5.0103260	3.9655100	0.3047700
H	3.4440690	4.6558310	0.6429420
H	4.3706850	5.6190700	-1.4561870
H	4.5156950	4.0077210	-2.1659230
H	2.9232890	4.6824850	-1.8397790
Pt	0.0000170	0.0000170	-0.0005570

S3.8 BI

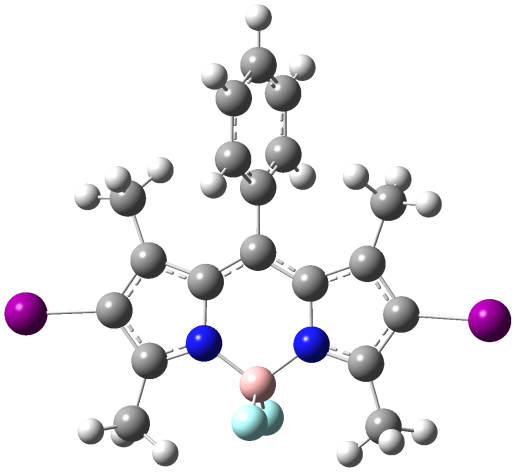

Figure S8: M06-2X/6-311+G(d)/aug-cc-pVTZ-PP optimized ground state geometry of BI in MeCN modelled by IEFPCM.

	X	Y	Z
C	2.5125690	-1.5680790	-0.0630580
C	2.5646670	0.7136720	0.0370360
C	3.3489840	-0.4329380	-0.0059440
C	1.2181060	0.2432060	-0.0120490
C	-0.0000010	0.9303690	0.0000540
C	-1.2181300	0.2432370	0.0121610
C	-2.5646890	0.7137170	-0.0369610
C	-3.3490190	-0.4328860	0.0059500
C	-2.5126210	-1.5680340	0.0631440
N	1.2419060	-1.1515650	-0.0626560
N	-1.2419530	-1.1515350	0.0628260
B	-0.0000320	-2.0734740	0.0001230
F	-0.0713540	-2.8845140	-1.1383130
F	0.0712770	-2.8844210	1.1386270
C	3.0731400	2.1170200	0.1289940
H	3.0795040	2.5972640	-0.8528040
H	2.4616200	2.7320910	0.7883540
H	4.0963690	2.1138640	0.5053640
C	-2.9188350	-2.9995580	0.0938860
H	-3.7053040	-3.1488410	0.8361710
H	-3.3267120	-3.2938650	-0.8772700
H	-2.0788710	-3.6481470	0.3300390
C	-3.0731640	2.1170620	-0.1289640
H	-2.4616400	2.7321150	-0.7883370
H	-4.0963880	2.1138900	-0.5053460
H	-3.0795430	2.5973360	0.8528180
C	2.9187670	-2.9996080	-0.0938290
H	2.0787770	-3.6481930	-0.3298990
H	3.7051670	-3.1489050	-0.8361840
H	3.3267300	-3.2939110	0.8772930
C	0.0000440	2.4153410	0.0000450
C	-0.3223730	3.1111480	1.1645630
C	0.3225410	3.1111010	-1.1644780
C	-0.3139530	4.5017940	1.1650760
H	-0.5743090	2.5618600	2.0658350
C	0.3142350	4.5017490	-1.1650150
H	0.5744420	2.5617770	-2.0657380
C	0.0001660	5.1976810	0.0000230
H	-0.5566540	5.0417080	2.0730760
H	0.5569880	5.0416270	-2.0730220
H	0.0002130	6.2816040	0.0000150
I	-5.4186950	-0.5403400	-0.0207690
I	5.4186610	-0.5404100	0.0206030

S3.9 BI-1

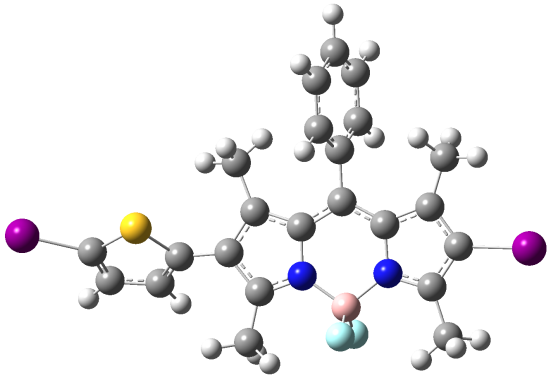

Figure S9: M06-2X/6-311+G(d)/aug-cc-pVTZ-PP optimized ground state geometry of BI-1 in toluene modelled by IEFPCM.

	X	Y	Z
C	1.0299920	-1.6789810	0.2244370
C	1.1337780	0.5888910	0.3475930
C	1.9084960	-0.5728110	0.3546400
C	-0.2165240	0.1608660	0.1975220
C	-1.4165610	0.8760870	0.1448090
C	-2.6494840	0.2203770	0.0701690
C	-3.9796160	0.7264430	-0.0482750
C	-4.7899190	-0.3999760	-0.0978160
C	-3.9833140	-1.5575950	-0.0279320
N	-0.2238510	-1.2322970	0.1349070
N	-2.7087400	-1.1736850	0.0728200
B	-1.4839910	-2.1293740	0.0485430
F	-1.4894770	-2.8608430	-1.1403390
F	-1.5145550	-3.0006690	1.1372690
C	1.6679360	1.9768710	0.5275970
H	1.7974550	2.4853170	-0.4317010
H	1.0054510	2.5947950	1.1327740
H	2.6425120	1.9351330	1.0156730
C	-4.4218200	-2.9788430	-0.0815530
H	-5.2328190	-3.1469110	0.6301950
H	-4.8082460	-3.2110650	-1.0778620
H	-3.6026980	-3.6571960	0.1430250
C	-4.4488160	2.1450750	-0.1174840
H	-3.7990980	2.7632580	-0.7367940
H	-5.4578340	2.1795980	-0.5288830
H	-4.4790630	2.5990340	0.8761940
C	1.3743530	-3.1277690	0.1953260
H	0.6770880	-3.6800060	-0.4334070
H	2.3900070	-3.2646620	-0.1760580
H	1.3185000	-3.5514830	1.2021860
C	-1.3776400	2.3606320	0.1627720
C	-1.7421100	3.0562140	1.3146620
C	-0.9713160	3.0580810	-0.9739360
C	-1.6947210	4.4457160	1.3304470
H	-2.0546170	2.5047300	2.1955890
C	-0.9395440	4.4482320	-0.9604310
H	-0.6881270	2.5080430	-1.8655090
C	-1.2974800	5.1426200	0.1921380
H	-1.9698000	4.9848880	2.2297660
H	-0.6331520	4.9893840	-1.8484440
C	3.3597370	-0.6893200	0.4833110
C	4.0712200	-1.5174920	1.3071900
S	4.4354700	0.2273010	-0.5337760
C	5.4830100	-1.4148340	1.1427220
H	3.5971090	-2.1748590	2.0256460
C	5.8211750	-0.5064150	0.1853140
H	6.2085110	-1.9792610	1.7124820
H	-1.2670420	6.2261100	0.2032530
I	7.7383810	0.0230370	-0.3935430
I	-6.8544610	-0.4583520	-0.2599700

S3.10 BI-2

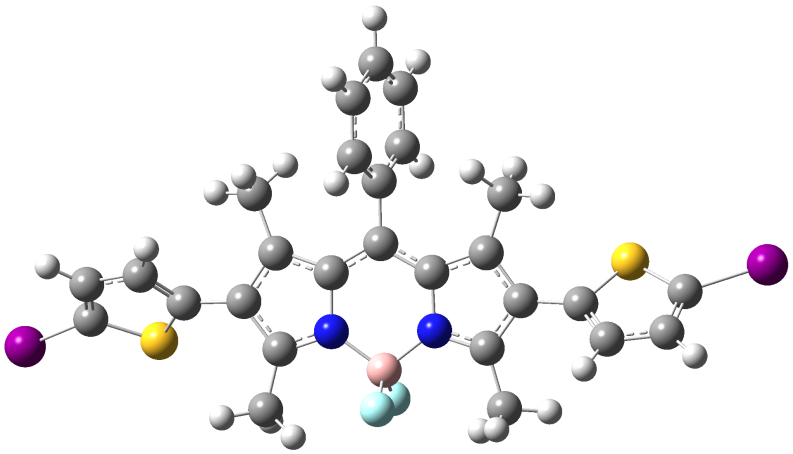

Figure S10: M06-2X/6-311+G(d)/aug-cc-pVTZ-PP optimized ground state geometry of BI-2 in toluene modelled by IEFPCM.

	X	Y	Z
C	2.3686070	-1.5717420	0.5237800
C	2.6187210	0.6855760	0.4245200
C	3.3193000	-0.5203350	0.4875470
C	1.2378700	0.3380240	0.4055700
C	0.0828640	1.1256920	0.3658570
C	-1.1891470	0.5493510	0.4277570
C	-2.4905120	1.1213890	0.3337330
C	-3.3885800	0.0570960	0.4356890
C	-2.6321350	-1.1354070	0.5692560
N	1.1406340	-1.0519280	0.4751560
N	-1.3331210	-0.8321110	0.5654470
B	-0.1751880	-1.8648420	0.5795010
F	-0.3139850	-2.7294830	-0.5070240
F	-0.1733540	-2.5992940	1.7670090
C	3.2499090	2.0440720	0.4436690
H	3.3250360	2.4700190	-0.5602230
H	2.6818610	2.7479350	1.0511640
H	4.2588940	1.9736750	0.8518760
C	-3.1367490	-2.5329760	0.6860970
H	-4.0920890	-2.5462270	1.2116830
H	-3.2927390	-2.9650020	-0.3066260
H	-2.4242920	-3.1622190	1.2163600
C	-2.8783520	2.5501340	0.1099920
H	-2.2098600	3.0493250	-0.5911470
H	-3.8945350	2.5937280	-0.2839480
H	-2.8558610	3.1253870	1.0394600
C	2.6240540	-3.0360580	0.6176720
H	1.8489850	-3.5995480	0.1000730
H	3.5988070	-3.2741600	0.1915220
H	2.6225540	-3.3541270	1.6641660
C	0.2100160	2.5999330	0.2515320
C	-0.0435290	3.4106120	1.3570320
C	0.5811540	3.1752710	-0.9628260
C	0.0795730	4.7913810	1.2487510
H	-0.3318930	2.9551260	2.2989760
C	0.6885010	4.5572680	-1.0726700
H	0.7791070	2.5377740	-1.8185390
C	0.4414920	5.3661700	0.0333950
H	-0.1115810	5.4185980	2.1121430
H	0.9684350	5.0023190	-2.0207010
C	-4.8467300	0.1496040	0.4190700
C	-5.6446100	1.0153060	1.1160880
S	-5.8122250	-0.8631970	-0.6181610
C	-7.0339730	0.8674540	0.8366970
H	-5.2456440	1.7301120	1.8254180
C	-7.2686950	-0.1141650	-0.0786000
H	-7.8174340	1.4518910	1.2999600
C	4.7674230	-0.7186610	0.5166620
C	5.5037810	-1.4839830	1.3784540
S	5.7952220	-0.0078700	-0.6951560
C	6.8991400	-1.4959030	1.0857530
H	5.0589710	-2.0146610	2.2114370
C	7.1976440	-0.7368200	-0.0057070
H	7.6407770	-2.0331270	1.6616120
H	0.5304930	6.4433160	-0.0517540
I	9.0741270	-0.4076530	-0.8197920
I	-9.1129720	-0.7336920	-0.7903970

S3.11 $[Ru(bpy)_3]^{2+}$

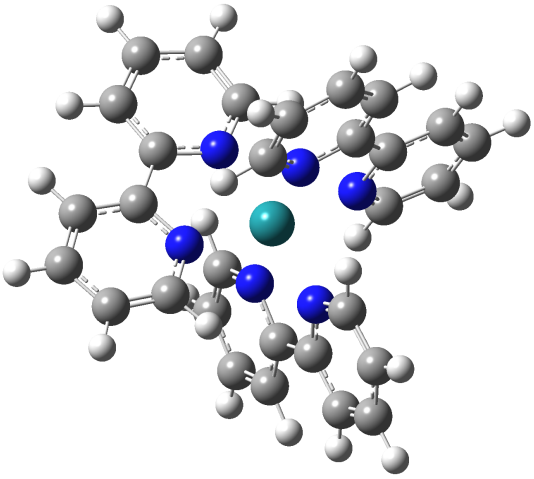

Figure S11: M06-L/6-311+G(d)/aug-cc-pVTZ-PP optimized ground state geometry of $[Ru(bpy)_3]^{2+}$ in MeCN modelled by IEFPCM.

	X	Y	Z
C	0.6554700	2.8136760	0.5734200
C	-0.9121190	2.0335330	2.1107700
C	0.6471370	4.0678410	1.1796690
C	1.4796190	2.4738780	-0.5848950
C	-0.9602750	3.2583890	2.7524520
H	-1.5133050	1.1952570	2.4499440
C	-0.1655960	4.2962980	2.2783610
H	1.2736890	4.8635450	0.7917100
C	2.3515440	3.3645290	-1.2071030
H	-1.6141580	3.3879020	3.6084470
H	-0.1783240	5.2707070	2.7570530
C	2.0608540	0.8057330	-2.1044560
C	3.0897710	2.9520890	-2.3046680
H	2.4527460	4.3772620	-0.8323990
C	2.9410840	1.6471380	-2.7612890
H	1.9108480	-0.2190730	-2.4304820
H	3.7715320	3.6397800	-2.7956070
H	3.4975210	1.2769180	-3.6158760
C	2.1066210	-1.9709970	0.5853770
C	2.1957610	-0.2283180	2.1298200
C	3.1916280	-2.5911440	1.2006050
C	1.4106420	-2.5132930	-0.5797870
C	3.2745690	-0.7999640	2.7810100
H	1.7637720	0.7087290	2.4685520
C	3.7831050	-2.0044370	2.3076650
H	3.5730250	-3.5302560	0.8146600
C	1.7601750	-3.7057480	-1.2094550
H	3.7032430	-0.3017720	3.6442060
H	4.6286590	-2.4812820	2.7938960
C	-0.3202320	-2.1875920	-2.1056230
C	1.0435380	-4.1373830	-2.3139410
H	2.5910310	-4.2940200	-0.8356990
C	-0.0178120	-3.3630110	-2.7694320
H	-1.1366280	-1.5500570	-2.4313410
H	1.3102540	-5.0646060	-2.8117260
H	-0.6103190	-3.6586010	-3.6288330
C	-2.7648690	-0.8415220	0.5769300
C	-1.3028630	-1.7824300	2.1284560
C	-3.8445240	-1.4745930	1.1886570
C	-2.8840920	0.0315490	-0.5890110
C	-2.3372930	-2.4333860	2.7768520
H	-0.2762470	-1.8734450	2.4704100
C	-3.6333850	-2.2775830	2.2979180
H	-4.8468840	-1.3396490	0.7969670
C	-4.0904280	0.3265650	-1.2200820
H	-2.1211610	-3.0513700	3.6419820
H	-4.4689200	-2.7745210	2.7813320
C	-1.7327780	1.3696920	-2.1103960
C	-4.1031560	1.1649590	-2.3231230
H	-5.0164690	-0.0986610	-0.8486190
C	-2.9008960	1.6974930	-2.7754390
H	-0.7713790	1.7572650	-2.4338660
H	-5.0383830	1.3993200	-2.8223070
H	-2.8594310	2.3598040	-3.6337700
N	-1.7086960	0.5521430	-1.0422470
N	-1.4972460	-0.9986490	1.0526250
N	0.3724050	-1.7567470	-1.0356260
N	1.6125680	-0.7908500	1.0559720
N	-0.1245820	1.8003850	1.0454180
N	1.3370550	1.1970680	-1.0401400
Ru	-0.0021010	0.0005820	0.0089490

S3.12 $Ir(ppy)_3$

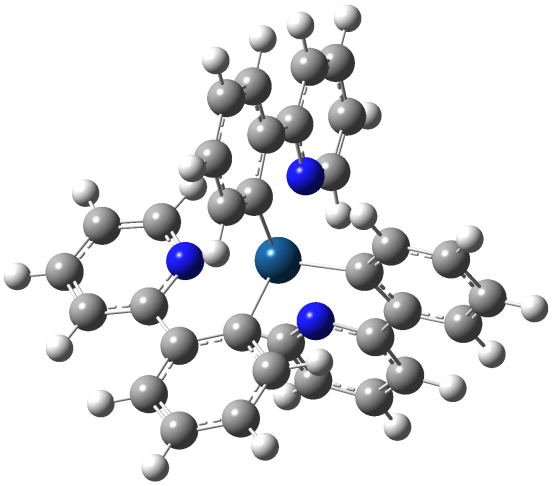

Figure S12: M06-L/6-311+G(d)/aug-cc-pVTZ-PP optimized ground state geometry of $Ir(ppy)_3$ in DCM modelled by IEFPCM.

	X	Y	Z
C	-2.1895150	-1.8767150	0.5770880
C	-0.4461430	-2.1369040	2.2147090
C	-2.9363290	-2.8725120	1.2247790
C	-2.6741820	-1.1928150	-0.6158460
C	-1.1905310	-3.1232340	2.8522430
H	0.5253080	-1.8640320	2.6260880
C	-2.4439900	-3.4954470	2.3607750
H	-3.9130960	-3.1650380	0.8425090
C	-3.8874860	-1.4494520	-1.2649340
H	-0.7944970	-3.6086220	3.7436710
H	-3.0280320	-4.2648580	2.8603980
C	-2.1800400	0.4536970	-2.1994490
C	-4.2349970	-0.7359420	-2.3987870
H	-4.5560440	-2.2115070	-0.8764770
C	-3.3647770	0.2395780	-2.8814550
H	-1.4638880	1.2041100	-2.5290500
H	-5.1769110	-0.9355660	-2.9035410
H	-3.5974270	0.8260680	-3.7647030
C	-0.5371480	2.8255410	0.5943050
C	-1.6509220	1.4329410	2.2095050
C	-1.0332220	3.9649220	1.2457700
C	0.3093500	2.9132620	-0.5897320
C	-2.1406400	2.5656960	2.8504170
H	-1.9048720	0.4519130	2.6102970
C	-1.8310220	3.8410990	2.3722920
H	-0.7942610	4.9601640	0.8742470
C	0.6996750	4.0976860	-1.2256230
H	-2.7692000	2.4582110	3.7338380
H	-2.2104940	4.7275950	2.8751350
C	1.5074090	1.6756140	-2.1692810
C	1.5042460	4.0514920	-2.3508110
H	0.3691430	5.0542180	-0.8326850
C	1.9208560	2.8141230	-2.8378270
H	1.8054420	0.6833480	-2.5026450
H	1.8070880	4.9711130	-2.8451440
H	2.5553270	2.7294140	-3.7144900
C	2.7131040	-0.9545890	0.6072080
C	2.0409330	0.6758390	2.2439110
C	3.9398280	-1.1049700	1.2712800
C	2.3804480	-1.7113360	-0.5938100
C	3.2589050	0.5234520	2.8974320
H	1.3114790	1.3769290	2.6489870
C	4.2161330	-0.3721110	2.4147540
H	4.6872340	-1.8029280	0.8971160
C	3.2222650	-2.6222040	-1.2427490
H	3.4680370	1.1053310	3.7945200
H	5.1671640	-0.4947410	2.9278050
C	0.7240690	-2.1076620	-2.1948150
C	2.7932100	-3.2738540	-2.3859510
H	4.2144870	-2.8156180	-0.8468550
C	1.5152840	-3.0143680	-2.8775490
H	-0.2836720	-1.8692570	-2.5297120
H	3.4472630	-3.9801740	-2.8910610
H	1.1356440	-3.5048790	-3.7683330
N	1.1351210	-1.4668380	-1.0902550
N	0.7225550	1.7113280	-1.0819600
N	-1.8334110	-0.2374630	-1.1032560
Ir	-0.0005600	-0.0023460	0.0324410
C	-0.8295800	1.5155140	1.0712440
C	1.7175950	-0.0561870	1.0877850
C	-0.9141140	-1.4734500	1.0665280

S3.13 PPO

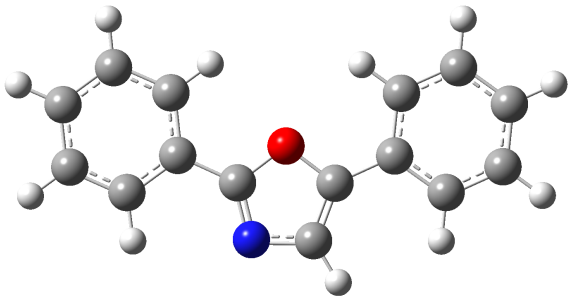

Figure S13: M06-2X/6-311+G(d) optimized ground state geometry of PPO in benzene modelled by IEFPCM.

	X	Y	Z
C	-1.0766780	-0.7392130	0.0001670
C	0.6122300	-2.0217320	0.0003630
C	1.0884920	-0.7481260	0.0001240
O	0.0002070	0.0765100	0.0002840
H	1.1622740	-2.9490860	0.0004380
N	-0.7680310	-1.9975780	-0.0001100
C	2.4141310	-0.1428020	0.0000120
C	2.5634750	1.2469170	-0.0002630
C	3.5551310	-0.9535460	0.0002060
C	3.8325580	1.8138330	-0.0003620
H	1.6841490	1.8802270	-0.0003940
C	4.8192470	-0.3820150	0.0000880
H	3.4518010	-2.0332730	0.0004500
C	4.9636620	1.0039030	-0.0001950
H	3.9370670	2.8929010	-0.0005760
H	5.6960400	-1.0196470	0.0002280
H	5.9525670	1.4476920	-0.0002770
C	-2.4056760	-0.1307210	0.0000710
C	-2.5571670	1.2574990	0.0002730
C	-3.5340270	-0.9554440	-0.0002560
C	-3.8299390	1.8151910	0.0001520
H	-1.6808310	1.8950710	0.0005280
C	-4.8020380	-0.3913690	-0.0003670
H	-3.4015770	-2.0310130	-0.0004230
C	-4.9535560	0.9938030	-0.0001650
H	-3.9444800	2.8930860	0.0003110
H	-5.6758680	-1.0329130	-0.0006250
H	-5.9456590	1.4308460	-0.0002590

S3.14 DPA

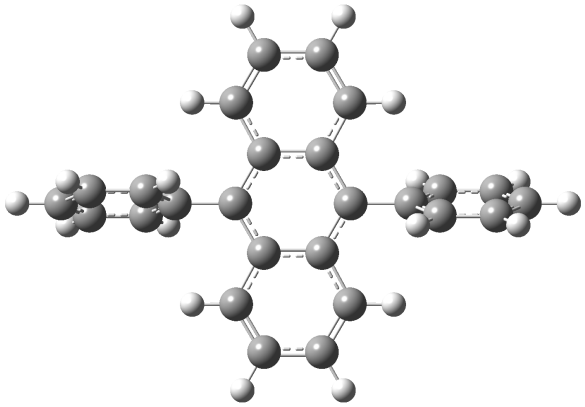

Figure S14: M06-2X/6-311+G(d) optimized ground state geometry of DPA in PhCl modelled by IEFPCM.

	X	Y	Z
C	0.7118270	-3.6540730	-0.0244240
C	1.4002150	-2.4788610	-0.0368910
C	0.7185370	-1.2174180	-0.0065570
C	-0.7185390	-1.2174180	0.0064030
C	-1.4002190	-2.4788630	0.0365950
C	-0.7118330	-3.6540750	0.0239950
C	1.4197790	-0.0000010	-0.0000100
C	-1.4197790	0.0000010	-0.0000070
C	-0.7185370	1.2174190	-0.0064220
C	0.7185390	1.2174170	0.0065340
C	1.4002190	2.4788590	0.0368640
H	2.4830280	2.4862700	0.0727420
C	0.7118340	3.6540720	0.0243970
C	-0.7118260	3.6540760	-0.0240190
C	-1.4002140	2.4788660	-0.0366150
H	1.2468630	-4.5967310	-0.0496230
H	2.4830230	-2.4862750	-0.0727700
H	-2.4830270	-2.4862790	0.0724750
H	-1.2468710	-4.5967340	0.0490860
H	1.2468720	4.5967290	0.0495930
H	-1.2468620	4.5967360	-0.0491110
H	-2.4830220	2.4862840	-0.0724930
C	-2.9118470	0.0000020	0.0000040
C	-3.6198630	0.2996810	1.1655310
C	-3.6198850	-0.2996760	-1.1655100
C	-5.0116930	0.2988640	1.1666120
H	-3.0734800	0.5350630	2.0733890
C	-5.0117160	-0.2988610	-1.1665630
H	-3.0735200	-0.5350570	-2.0733790
C	-5.7104180	0.0000010	0.0000310
H	-5.5500140	0.5312460	2.0787520
H	-5.5500550	-0.5312430	-2.0786930
H	-6.7945590	0.0000000	0.0000420
C	2.9118470	-0.0000020	-0.0000030
C	3.6198820	0.2997880	-1.1654900
C	3.6198650	-0.2997930	1.1654940
C	5.0117120	0.2989730	-1.1665480
H	3.0735130	0.5352540	-2.0733350
C	5.0116960	-0.2989760	1.1665720
H	3.0734830	-0.5352590	2.0733310
C	5.7104170	-0.0000020	0.0000170
H	5.5500500	0.5314400	-2.0786560
H	5.5500210	-0.5314440	2.0786870
H	6.7945580	-0.0000010	0.0000250

S3.15 Perylene

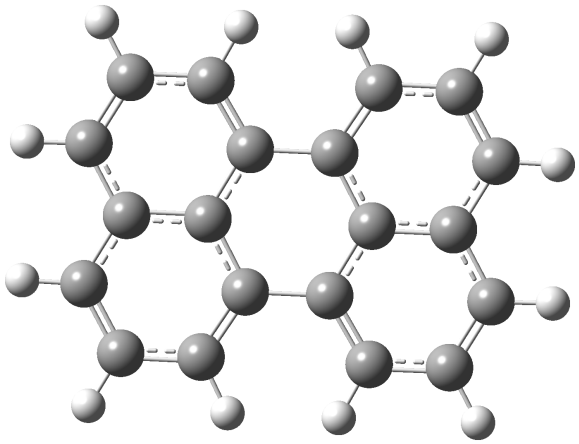

Figure S15: M06-2X/6-311+G(d) optimized ground state geometry of perylene in MeCN modelled by IEFPCM.

	X	Y	Z
C	0.0000000	2.4152280	2.8806720
C	0.0000000	1.2301950	3.5666410
C	0.0000000	0.0000000	2.8637410
C	0.0000000	0.0000000	1.4383260
C	0.0000000	1.2476870	0.7397650
C	0.0000000	2.4199600	1.4730960
H	0.0000000	-1.2140850	4.6514590
H	0.0000000	3.3587560	3.4142170
H	0.0000000	1.2140850	4.6514590
C	0.0000000	-1.2301950	3.5666410
C	0.0000000	-1.2476870	0.7397650
H	0.0000000	3.3804670	0.9748150
C	0.0000000	-2.4199600	1.4730960
C	0.0000000	-2.4152280	2.8806720
H	0.0000000	-3.3804670	0.9748150
H	0.0000000	-3.3587560	3.4142170
C	0.0000000	-1.2476870	-0.7397650
C	0.0000000	0.0000000	-1.4383260
C	0.0000000	-2.4199600	-1.4730960
C	0.0000000	1.2476870	-0.7397650
C	0.0000000	0.0000000	-2.8637410
C	0.0000000	-2.4152280	-2.8806720
H	0.0000000	-3.3804670	-0.9748150
C	0.0000000	2.4199600	-1.4730960
C	0.0000000	1.2301950	-3.5666410
C	0.0000000	-1.2301950	-3.5666410
H	0.0000000	-3.3587560	-3.4142170
C	0.0000000	2.4152280	-2.8806720
H	0.0000000	3.3804670	-0.9748150
H	0.0000000	1.2140850	-4.6514590
H	0.0000000	-1.2140850	-4.6514590
H	0.0000000	3.3587560	-3.4142170

S3.16 1-CBPEA

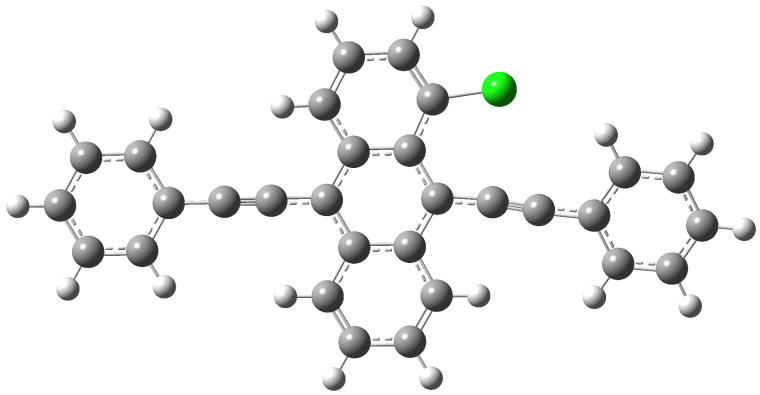

Figure S16: M06-2X/6-311+G(d) optimized ground state geometry of 1-CBPEA in MeCN modelled by IEFPCM.

	X	Y	Z
C	-0.9077860	-3.7346590	-0.2095990
C	-1.5998180	-2.5622220	-0.1572270
C	-0.9171420	-1.3079110	-0.1242050
C	0.5091850	-1.2883840	-0.1475760
C	1.1963620	-2.5416600	-0.1926980
C	0.5137340	-3.7216750	-0.2267640
C	-1.6209060	-0.0895250	-0.0494190
C	1.2137080	-0.0536350	-0.1234260
C	0.5060620	1.1760510	-0.1189650
C	-0.9334750	1.1444110	-0.0424400
C	-1.6794210	2.3581170	0.0449440
H	-2.7580300	2.2974520	0.1171210
C	-1.0580340	3.5666750	0.0367350
C	0.3496430	3.6300370	-0.0965990
C	1.0949820	2.4910860	-0.1816610
H	-1.4378440	-4.6796190	-0.2372070
H	-2.6830950	-2.5640110	-0.1405240
H	2.2780390	-2.5449740	-0.2060630
H	1.0577030	-4.6583130	-0.2682340
H	-1.6274580	4.4854410	0.1074700
H	0.8448570	4.5913730	-0.1523950
C	2.6343700	-0.1454940	-0.0520640
C	-3.0435600	-0.1080780	0.0130750
C	3.8216830	-0.3462160	0.0459170
C	-4.2507720	-0.1351970	0.0629370
C	5.2388550	-0.4891620	0.1525470
C	6.0270200	0.6202880	0.4927150
C	5.8545620	-1.7265970	-0.0829310
C	7.4057890	0.4894990	0.5941030
H	5.5489370	1.5757540	0.6767430
C	7.2341650	-1.8482020	0.0202030
H	5.2463120	-2.5842190	-0.3475220
C	8.0123860	-0.7426160	0.3579850
H	8.0085660	1.3506750	0.8589750
H	7.7037340	-2.8079660	-0.1625770
H	9.0889790	-0.8416440	0.4379370
C	-5.6782910	-0.1661420	0.1164020
C	-6.3572130	-1.3927470	0.1197090
C	-6.4099120	1.0292260	0.1619530
C	-7.7448710	-1.4189430	0.1671390
H	-5.7900180	-2.3160040	0.0847570
C	-7.7973850	0.9934410	0.2093010
H	-5.8831860	1.9768160	0.1591170
C	-8.4672450	-0.2282470	0.2117140
H	-8.2642790	-2.3702390	0.1690440
H	-8.3574830	1.9207640	0.2437270
H	-9.5502840	-0.2524210	0.2481110
Cl	2.8055590	2.7477650	-0.4470180

S3.17 Pyrene

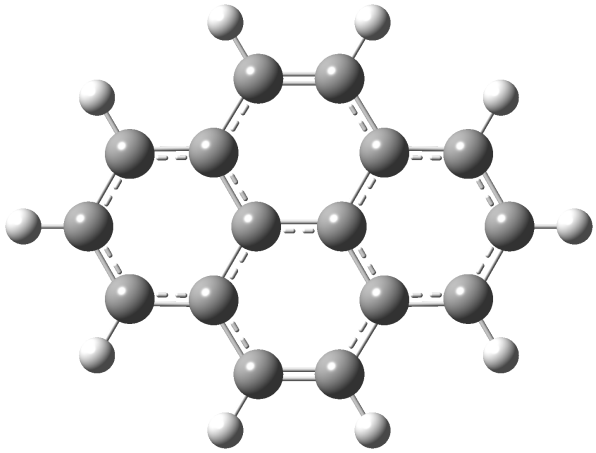

Figure S17: M06-2X/6-311+G(d) optimized ground state geometry of pyrene in DCM modelled by IEFPCM.

	X	Y	Z
C	3.5126090	-0.0000100	0.0003320
C	2.8231540	-1.2077900	0.0002780
C	1.4242830	-1.2297420	0.0001590
C	0.7140090	-0.0000010	0.0000860
C	1.4242960	1.2297430	0.0001560
C	2.8231510	1.2077870	0.0002790
C	0.6766860	-2.4619350	0.0001100
C	-0.7140090	-0.0000020	-0.0000640
C	-1.4242850	-1.2297400	-0.0001240
C	-0.6766910	-2.4619330	-0.0000220
C	-2.8231590	-1.2077870	-0.0002860
H	-3.3683650	-2.1460120	-0.0003360
C	-3.5126080	-0.0000070	-0.0003900
C	-2.8231470	1.2077910	-0.0003260
C	-1.4242930	1.2297460	-0.0001610
C	-0.6766830	2.4619400	-0.0000840
C	0.6766880	2.4619390	0.0000760
H	1.2278990	3.3967740	0.0001440
H	-1.2278900	3.3967770	-0.0001560
H	1.2278980	-3.3967690	0.0001810
H	4.5966740	-0.0000020	0.0004080
H	3.3683650	-2.1460130	0.0003200
H	3.3683720	2.1460040	0.0003250
H	-1.2278970	-3.3967710	-0.0000570
H	-4.5966740	0.0000080	-0.0005210
H	-3.3683780	2.1460020	-0.0004130

S3.18 BA

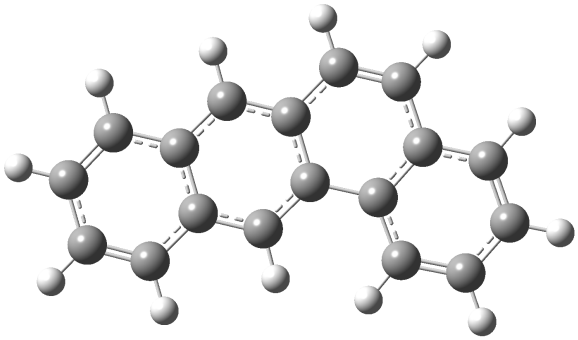

Figure S18: M06-2X/6-311+G(d) optimized ground state geometry of BA in toluene modelled by IEFPCM.

	X	Y	Z
C	-4.3497950	-1.3760260	-0.0003390
C	-3.0276250	-1.7166300	-0.0003990
C	-2.0159120	-0.7113210	-0.0001140
C	-2.4098240	0.6597960	0.0001490
C	-3.7993710	0.9802090	0.0002260
C	-4.7414380	-0.0077180	0.0000050
C	-0.6485690	-1.0349960	-0.0001080
C	-1.4112200	1.6440720	0.0002690
C	-0.0637390	1.3155480	0.0002100
C	0.3392000	-0.0615210	0.0001130
C	2.2549710	2.0494750	-0.0002310
C	0.9420410	2.3513870	0.0000850
H	-5.1108500	-2.1480790	-0.0005470
H	-2.7263230	-2.7594620	-0.0006760
H	-4.0931910	2.0250450	0.0004910
H	-5.7957520	0.2446910	0.0000800
H	3.0029110	2.8358280	-0.0003560
H	0.6106180	3.3848410	0.0002260
H	-1.7004340	2.6913560	0.0003560
H	-0.3870860	-2.0867890	-0.0003570
C	2.7097480	0.6782410	-0.0002500
C	4.0871880	0.3898890	-0.0005150
C	1.7705290	-0.3781450	0.0001660
C	4.5394070	-0.9124770	-0.0002350
H	4.7927200	1.2148490	-0.0009210
C	2.2576410	-1.6985660	0.0005970
C	3.6128910	-1.9636220	0.0004090
H	5.6027600	-1.1228380	-0.0004700
H	1.5689450	-2.5340240	0.0011680
H	3.9589370	-2.9909830	0.0007890

S3.19 DBP

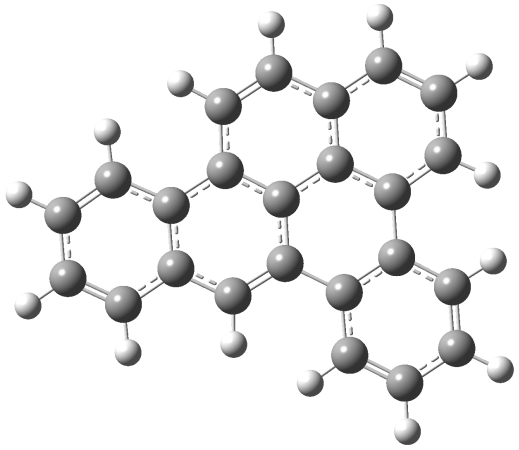

Figure S19: M06-2X/6-311+G(d) optimized ground state geometry of DBP in toluene modelled by IEFPCM.

	X	Y	Z
C	-1.2746920	-1.7082780	-0.0005210
C	-0.1094710	-0.9829130	-0.0002870
C	-0.1929570	0.4535800	0.0000410
C	-1.4487230	1.0944050	0.0001400
C	1.0126180	1.2364990	0.0001780
C	2.2932790	0.6171360	0.0001710
C	3.4239210	1.4273650	0.0003100
H	4.4129400	0.9900330	0.0002760
C	3.3303140	2.8218110	0.0004760
C	2.0961480	3.4320470	0.0004910
C	0.9265180	2.6535090	0.0003470
C	-0.3609820	3.2700900	0.0003280
C	-1.4929290	2.5256530	0.0002390
H	-2.4477850	3.0335980	0.0001720
H	-0.4163540	4.3539060	0.0003630
H	-1.2576100	-2.7907780	-0.0008270
H	4.2359520	3.4176600	0.0005810
H	2.0109680	4.5138030	0.0006130
C	2.3863650	-0.8522120	-0.0000320
C	3.6331530	-1.5048260	0.0000710
C	1.2133650	-1.6325640	-0.0003410
C	3.7315560	-2.8809240	-0.0001960
H	4.5488610	-0.9292410	0.0003730
C	1.3368670	-3.0343210	-0.0006360
C	2.5690030	-3.6549380	-0.0005940
H	4.7068400	-3.3540490	-0.0001060
H	0.4538540	-3.6588620	-0.0009030
H	2.6293180	-4.7372600	-0.0008380
C	-2.6588900	0.3143430	0.0000720
C	-3.9594880	0.8824860	0.0004290
C	-2.5522420	-1.0988080	-0.0003150
C	-5.0810730	0.0918500	0.0002930
H	-4.0878620	1.9568550	0.0008760
C	-3.7275720	-1.8949230	-0.0004850
C	-4.9680560	-1.3163140	-0.0001840
H	-6.0626470	0.5522800	0.0006010
H	-3.6217740	-2.9753390	-0.0008320
H	-5.8608870	-1.9311140	-0.0003120