

# Supporting Information:

## Spatial Contributions to $^1\text{H}$ NMR Chemical Shifts of Free-Base Porphyrinoids

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### S1 Optimized molecular geometries

#### S1.1 Free-base trans-porphyrin

38

H	1.1040146453	0.0000000000	0.0000000000
N	2.1352114913	0.0000000000	0.0000000000
C	2.9180354650	-1.1345237048	0.0000000000
C	2.9180354650	1.1345237048	0.0000000000
C	4.2915746137	-0.6919362118	0.0000000000
C	4.2915746137	0.6919362118	0.0000000000
H	5.1596090171	-1.3639029600	0.0000000000
H	5.1596090171	1.3639029600	0.0000000000
C	2.4374187734	-2.4538971596	0.0000000000
H	3.2039598564	-3.2453519248	0.0000000000
H	-1.1040146453	0.0000000000	0.0000000000
N	0.0000000000	-2.0395485771	0.0000000000
N	-2.1352114913	0.0000000000	0.0000000000
N	0.0000000000	2.0395485771	0.0000000000
C	-1.0895128344	-2.8696821891	0.0000000000
C	-2.9180354650	1.1345237048	0.0000000000
C	1.0895128344	2.8696821891	0.0000000000
C	1.0895128344	-2.8696821891	0.0000000000
C	-2.9180354650	-1.1345237048	0.0000000000
C	-1.0895128344	2.8696821891	0.0000000000
C	-0.6846007936	-4.2795792989	0.0000000000
C	-4.2915746137	0.6919362118	0.0000000000
C	0.6846007936	4.2795792989	0.0000000000
C	0.6846007936	-4.2795792989	0.0000000000

C	-4.2915746137	-0.6919362118	0.0000000000
C	-0.6846007936	4.2795792989	0.0000000000
H	-1.3668637177	-5.1413680988	0.0000000000
H	-5.1596090171	1.3639029600	0.0000000000
H	1.3668637177	5.1413680988	0.0000000000
H	1.3668637177	-5.1413680988	0.0000000000
H	-5.1596090171	-1.3639029600	0.0000000000
H	-1.3668637177	5.1413680988	0.0000000000
C	-2.4374187734	-2.4538971596	0.0000000000
C	-2.4374187734	2.4538971596	0.0000000000
C	2.4374187734	2.4538971596	0.0000000000
H	-3.2039598564	-3.2453519248	0.0000000000
H	-3.2039598564	3.2453519248	0.0000000000
H	3.2039598564	3.2453519248	0.0000000000

The Turbomole optimized molecular structure of trans-porphyrin as an xyz file<sup>?</sup>

## S1.2 Free-base isophlorin

40

H	1.2138256732	-0.0000040886	0.0000000000
N	2.2043019071	-0.0000013588	0.0000000000
C	2.9737728939	-1.1456166430	0.0000000000
C	2.9737694129	1.1456174978	0.0000000000
C	4.2928936622	-0.7055040197	0.0000000000
C	4.2928898846	0.7055117019	0.0000000000
H	5.1564212206	-1.3500760053	0.0000000000
H	5.1564138711	1.3500878120	0.0000000000
C	2.4532579269	-2.4862996891	0.0000000000
H	3.2068552443	-3.2622338070	0.0000000000
H	-1.2138175741	0.0000067477	0.0000000000
N	-0.0000100355	-2.1491476784	0.0000000000
N	-2.2042956084	0.0000006510	0.0000000000
N	-0.0000131723	2.1491495964	0.0000000000
C	-1.1626349216	-2.9192475043	0.0000000000
C	-2.9737707702	1.1456115322	0.0000000000
C	1.1626196733	2.9192530062	0.0000000000
C	1.1626214275	-2.9192533093	0.0000000000
C	-2.9737651535	-1.1456127622	0.0000000000
C	-1.1626363017	2.9192481383	0.0000000000
C	-0.6762877996	-4.2858840178	0.0000000000
C	-4.2928938349	0.7055014693	0.0000000000
C	0.6762780099	4.2858886202	0.0000000000
C	0.6762750619	-4.2858895495	0.0000000000
C	-4.2928893230	-0.7055118892	0.0000000000
C	-0.6762845107	4.2858862279	0.0000000000
H	-1.3261949616	-5.1463635747	0.0000000000
H	-5.1564173325	1.3500786452	0.0000000000
H	1.3261678366	5.1463807659	0.0000000000
H	1.3261629358	-5.1463836358	0.0000000000
H	-5.1564076023	-1.3500952179	0.0000000000
H	-1.3261905134	5.1463674718	0.0000000000
C	-2.4532698492	-2.4862970337	0.0000000000
C	-2.4532747707	2.4862985484	0.0000000000
C	2.4532529706	2.4862974170	0.0000000000
H	-3.2068725273	-3.2622234583	0.0000000000

H	-3.2068765965	3.2622273730	0.0000000000
H	3.2068490662	3.2622316338	0.0000000000
H	0.0000923528	1.1597831980	0.0000000000
H	0.0000821275	-1.1597828110	0.0000000000

The Turbomole optimized molecular structure of free-base isophlorin as an xyz file.

### S1.3 Free-base trans-norcorrole

34

C	3.1367113581	-0.8563208715	-0.1178777568
C	2.8063639364	0.4813169136	-0.2490699976
C	3.5218041661	1.6759148983	0.1548604356
C	2.6191906019	2.7055849190	0.1391374747
C	1.3599478851	2.1334848836	-0.2938176428
C	-0.0388036217	2.5930464079	-0.2873394801
C	-0.7891639161	3.6551063861	0.2435836017
C	-2.1363653830	3.2426336262	0.2746414105
C	-2.1900279052	1.9270773414	-0.2310502327
C	-3.1367701681	0.8561707129	-0.1171749153
C	-2.8064723155	-0.4816056300	-0.2470334427
C	-3.5217281351	-1.6757697755	0.1585133213
C	-2.6191438235	-2.7054829877	0.1433994623
C	-1.3601074636	-2.1338542032	-0.2907766948
C	0.0386520435	-2.5933830086	-0.2843621853
C	0.7892760469	-3.6547670331	0.2475477276
C	2.1364886407	-3.2422621854	0.2773936062
C	2.1899297869	-1.9273707548	-0.2300379536
H	4.1345910223	-1.1078151781	0.2202885429
H	-4.1344767645	1.1080579170	0.2211917297
H	4.5580609323	1.7265969208	0.4520760096
H	2.7955397230	3.7309817895	0.4227480367
H	-0.4009695699	4.5946746997	0.5999811580
H	-2.9686568925	3.8090170672	0.6601853943
H	-4.5578242966	-1.7260679747	0.4563571801
H	-2.7953469302	-3.7305947544	0.4281380275
H	0.4012381063	-4.5938577191	0.6053854129
H	2.9689491736	-3.8081572420	0.6632934881
N	1.5094288709	0.8559689236	-0.5598721229
N	-0.9203672734	1.6328747021	-0.6202112142
N	-1.5096887547	-0.8566010065	-0.5580586132
N	0.9200594058	-1.6336341368	-0.6189342380
H	-0.6883963609	0.6631931954	-0.8317200828
H	0.6880778744	-0.6641568432	-0.8313854469

The Turbomole optimized molecular structure of trans-norcorrole as an xyz file.

## S2 Atomic contributions to magnetic shielding constants

The atomic contributions to the isotropic  $^1\text{H}$  NMR shielding constants calculated at the BHandHLYP level using the pcseg-3 basis sets.

## S2.1 Free-base trans-porphyrin

### S2.1.1 Inner hydrogen (atom 1)

$$\sigma_{xx} = 25.747313$$

$$\sigma_{yy} = 23.637856$$

$$\sigma_{zz} = 63.164402$$

shielding constant	=	37.516523
positive contribution	=	52.055053
negative contribution	=	-14.538530
sum	=	37.516523

atom contributions, total, positive, negative				
atom	1	12.854767	16.841950	-3.987183
atom	2	5.275998	7.067669	-1.791671
atom	3	2.351627	2.888484	-0.536857
atom	4	2.351627	2.888484	-0.536857
atom	5	0.951516	1.169492	-0.217976
atom	6	0.951516	1.169492	-0.217976
atom	7	0.213403	0.213890	-0.000487
atom	8	0.213403	0.213890	-0.000487
atom	9	1.538546	1.885742	-0.347196
atom	10	0.274250	0.274554	-0.000304
atom	11	-0.509123	0.009360	-0.518483
atom	12	-0.262820	1.232433	-1.495253
atom	13	0.170400	0.549085	-0.378685
atom	14	-0.262820	1.232433	-1.495253
atom	15	0.824887	1.044848	-0.219961
atom	16	0.574244	0.744414	-0.170170
atom	17	1.159747	1.629181	-0.469435
atom	18	1.159747	1.629181	-0.469435
atom	19	0.574244	0.744414	-0.170170
atom	20	0.824887	1.044848	-0.219961
atom	21	0.374798	0.498743	-0.123946
atom	22	0.336621	0.409544	-0.072923
atom	23	0.348623	0.490017	-0.141395
atom	24	0.348623	0.490017	-0.141395
atom	25	0.336621	0.409544	-0.072923
atom	26	0.374798	0.498743	-0.123946
atom	27	0.122865	0.123104	-0.000240
atom	28	0.091435	0.091782	-0.000347
atom	29	0.126149	0.128090	-0.001940
atom	30	0.126149	0.128090	-0.001940
atom	31	0.091435	0.091782	-0.000347
atom	32	0.122865	0.123104	-0.000240
atom	33	0.693450	0.826138	-0.132688
atom	34	0.693450	0.826138	-0.132688
atom	35	1.538546	1.885742	-0.347196
atom	36	0.142899	0.143036	-0.000137
atom	37	0.142899	0.143036	-0.000137
atom	38	0.274250	0.274554	-0.000304
sum		37.516523	52.055053	-14.538530

### S2.1.2 Meso hydrogen (atom 10)

$$\sigma_{xx} = 27.195053$$

$$\sigma_{yy} = 27.619085$$

$$\sigma_{zz} = 5.884763$$

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shielding constant   =      20.232967
positive contribution =      35.048321
negative contribution =     -14.815354
sum                  =      20.232967

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atom contributions, total, positive, negative

atom	1	0.115737	0.127140	-0.011403
atom	2	0.138256	0.408772	-0.270516
atom	3	-0.929038	0.803620	-1.732657
atom	4	0.297276	0.466793	-0.169517
atom	5	-0.268978	0.613149	-0.882127
atom	6	0.568199	0.710049	-0.141850
atom	7	0.088603	0.226327	-0.137724
atom	8	0.142518	0.143121	-0.000603
atom	9	-0.682782	4.355265	-5.038048
atom	10	18.397033	20.493397	-2.096364
atom	11	-0.078376	0.002582	-0.080958
atom	12	0.139076	0.477854	-0.338778
atom	13	0.028558	0.145283	-0.116724
atom	14	-0.026520	0.163506	-0.190027
atom	15	0.141664	0.378825	-0.237160
atom	16	0.188567	0.232137	-0.043570
atom	17	0.216537	0.303469	-0.086933
atom	18	-0.618970	0.914586	-1.533556
atom	19	0.173617	0.261689	-0.088072
atom	20	0.189006	0.240706	-0.051700
atom	21	0.477489	0.648714	-0.171225
atom	22	0.155555	0.186416	-0.030861
atom	23	0.077432	0.123742	-0.046311
atom	24	-0.251642	0.657806	-0.909448
atom	25	0.106413	0.146068	-0.039655
atom	26	0.117043	0.152975	-0.035932
atom	27	0.146194	0.146796	-0.000602
atom	28	0.044874	0.044935	-0.000060
atom	29	0.035461	0.038538	-0.003077
atom	30	0.078168	0.231983	-0.153815
atom	31	0.036541	0.039338	-0.002796
atom	32	0.044362	0.044437	-0.000075
atom	33	0.263013	0.332025	-0.069013
atom	34	0.210102	0.245248	-0.035146
atom	35	0.276649	0.340260	-0.063610
atom	36	0.072362	0.075347	-0.002985
atom	37	0.050763	0.050805	-0.000042
atom	38	0.072203	0.074618	-0.002415
sum		20.232967	35.048321	-14.815354

### S2.1.3 $\beta$ hydrogen in pyrrole ring with inner hydrogen (atom 7)

$$\sigma_{xx} = 24.445006$$

$$\sigma_{yy} = 26.417525$$

$$\sigma_{zz} = 11.765908$$

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shielding constant   =      20.876146
positive contribution =      33.681130
negative contribution =     -12.804984
sum                  =      20.876146

```

atom contributions, total, positive, negative				
atom	1	0.170976	0.171982	-0.001006
atom	2	-0.040733	0.467345	-0.508079
atom	3	-1.224128	0.664972	-1.889100
atom	4	0.027509	0.537962	-0.510453
atom	5	0.682943	5.034995	-4.352053
atom	6	0.938876	1.572872	-0.633997
atom	7	18.114521	20.196297	-2.081775
atom	8	0.335071	0.361500	-0.026430
atom	9	-0.449245	0.415662	-0.864906
atom	10	0.010865	0.183797	-0.172932
atom	11	-0.068103	0.000705	-0.068808
atom	12	0.023792	0.207372	-0.183580
atom	13	0.020770	0.105584	-0.084814
atom	14	-0.007380	0.157676	-0.165056
atom	15	0.142360	0.220555	-0.078194
atom	16	0.145060	0.184454	-0.039394
atom	17	0.175920	0.289053	-0.113133
atom	18	0.111407	0.356150	-0.244744
atom	19	0.139444	0.189876	-0.050431
atom	20	0.153723	0.205768	-0.052044
atom	21	0.190193	0.253672	-0.063479
atom	22	0.110337	0.132932	-0.022594
atom	23	0.043742	0.118875	-0.075133
atom	24	-0.013058	0.177952	-0.191010
atom	25	0.096765	0.120998	-0.024233
atom	26	0.130089	0.170524	-0.040435
atom	27	0.066993	0.067133	-0.000139
atom	28	0.033632	0.033733	-0.000101
atom	29	0.026747	0.037630	-0.010883
atom	30	0.016932	0.054934	-0.038002
atom	31	0.031080	0.031692	-0.000612
atom	32	0.047963	0.048028	-0.000065
atom	33	0.185377	0.222421	-0.037044
atom	34	0.177304	0.207777	-0.030473
atom	35	0.168761	0.297973	-0.129212
atom	36	0.048342	0.048755	-0.000413
atom	37	0.044368	0.044423	-0.000055
atom	38	0.066930	0.087102	-0.020172
sum		20.876146	33.681130	-12.804984

#### S2.1.4 $\beta$ hydrogen in pyrrole ring without inner hydrogen (atom 30)

$\sigma_{xx} = 26.135387$   
 $\sigma_{yy} = 23.742174$   
 $\sigma_{zz} = 13.325699$

shielding constant	=	21.067753
positive contribution	=	33.880014
negative contribution	=	-12.812261
sum	=	21.067753

atom contributions, total, positive, negative				
atom	1	0.005774	0.036234	-0.030460
atom	2	0.040836	0.195835	-0.154999
atom	3	-0.000270	0.287482	-0.287752
atom	4	0.192679	0.254495	-0.061816

atom	5	-0.005877	0.181888	-0.187765
atom	6	0.241180	0.295377	-0.054197
atom	7	0.020724	0.056838	-0.036114
atom	8	0.067065	0.067200	-0.000135
atom	9	-0.557483	0.401208	-0.958690
atom	10	0.001252	0.190857	-0.189606
atom	11	-0.039116	0.010593	-0.049709
atom	12	0.013669	0.590406	-0.576737
atom	13	0.026302	0.148211	-0.121909
atom	14	-0.023901	0.121450	-0.145351
atom	15	-0.294551	0.427724	-0.722275
atom	16	0.172108	0.213664	-0.041556
atom	17	0.162250	0.214770	-0.052520
atom	18	-1.358723	0.682401	-2.041124
atom	19	0.115996	0.238636	-0.122639
atom	20	0.156710	0.200089	-0.043379
atom	21	1.002172	1.660655	-0.658483
atom	22	0.169083	0.203575	-0.034492
atom	23	0.071507	0.100219	-0.028712
atom	24	1.486042	5.320623	-3.834580
atom	25	0.064441	0.130916	-0.066475
atom	26	0.082760	0.109290	-0.026529
atom	27	0.342473	0.366261	-0.023789
atom	28	0.048156	0.048213	-0.000057
atom	29	0.030556	0.031311	-0.000755
atom	30	18.101649	20.115889	-2.014239
atom	31	0.028555	0.038641	-0.010086
atom	32	0.033320	0.033452	-0.000132
atom	33	0.138099	0.285441	-0.147342
atom	34	0.180503	0.210640	-0.030137
atom	35	0.192344	0.227781	-0.035436
atom	36	0.066127	0.088030	-0.021903
atom	37	0.044595	0.044648	-0.000053
atom	38	0.048746	0.049073	-0.000326
sum		21.067753	33.880014	-12.812261

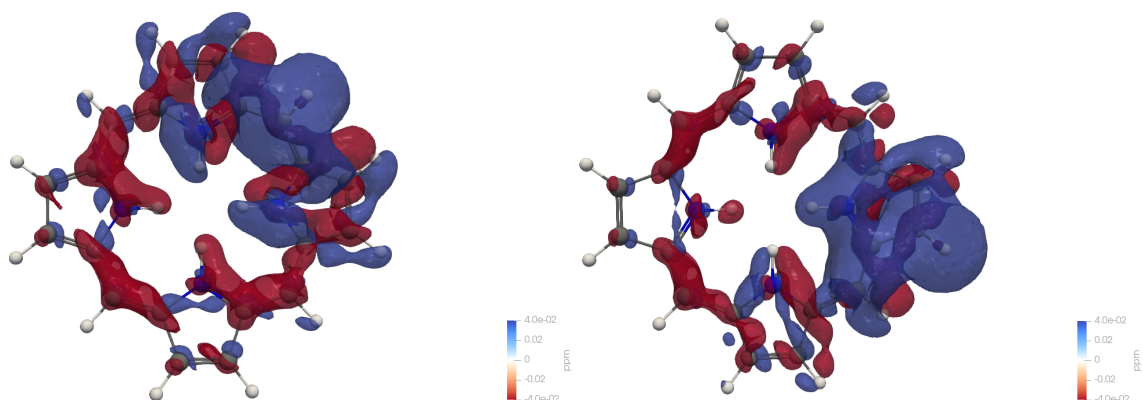


Figure S1: The isotropic  $^1\text{H}$  NMR shielding density of the *meso* and  $\beta$  hydrogens of free-base porphyrin. The shielding contributions are shown in blue and the deshielding contributions in red. An isovalue of  $\pm 0.04$  has been used.

## S2.2 Free-base isophlorin

### S2.2.1 Inner hydrogen (atom 1)

$\sigma_{xx} = 30.474650$   
 $\sigma_{yy} = 29.829815$   
 $\sigma_{zz} = -79.136229$

shielding constant	=	-6.277254
positive contribution	=	32.480035
negative contribution	=	-38.757290
sum	=	-6.277254

atom contributions, total, positive, negative				
atom	1	16.463637	20.274013	-3.810376
atom	2	0.964973	4.719532	-3.754559
atom	3	-2.184604	0.728758	-2.913362
atom	4	-2.184593	0.728755	-2.913348
atom	5	-0.488056	0.359010	-0.847065
atom	6	-0.488055	0.359009	-0.847065
atom	7	0.215735	0.216142	-0.000407
atom	8	0.215735	0.216142	-0.000407
atom	9	-2.379262	0.186858	-2.566120
atom	10	0.227185	0.228930	-0.001745
atom	11	-0.567747	0.001187	-0.568934
atom	12	-0.886423	0.418439	-1.304862
atom	13	-0.744443	0.140797	-0.885240
atom	14	-0.886411	0.418433	-1.304844
atom	15	-0.840370	0.219988	-1.060358
atom	16	-0.863906	0.112003	-0.975909
atom	17	-1.848414	0.199266	-2.047680
atom	18	-1.848424	0.199268	-2.047692
atom	19	-0.863909	0.112003	-0.975912
atom	20	-0.840369	0.219987	-1.060356
atom	21	-0.331904	0.145767	-0.477671
atom	22	-0.155775	0.117064	-0.272839
atom	23	-0.337927	0.166005	-0.503932
atom	24	-0.337930	0.166005	-0.503935
atom	25	-0.155775	0.117065	-0.272839
atom	26	-0.331902	0.145767	-0.477669
atom	27	0.107867	0.108266	-0.000400
atom	28	0.084510	0.084792	-0.000282
atom	29	0.109383	0.112701	-0.003318
atom	30	0.109384	0.112701	-0.003318
atom	31	0.084510	0.084792	-0.000282
atom	32	0.107866	0.108266	-0.000400
atom	33	-0.949249	0.075819	-1.025068
atom	34	-0.949247	0.075819	-1.025065
atom	35	-2.379254	0.186857	-2.566111
atom	36	0.112394	0.113151	-0.000756
atom	37	0.112394	0.113151	-0.000756
atom	38	0.227184	0.228929	-0.001745
atom	39	-0.788036	0.079298	-0.867334
atom	40	-0.788026	0.079301	-0.867327



### S2.2.2 Meso hydrogen (atom 10)

$$\sigma_{xx} = 29.180519$$

$$\sigma_{yy} = 28.447813$$

$$\sigma_{zz} = 45.746409$$

shielding constant	=	34.458247
positive contribution	=	46.551674
negative contribution	=	-12.093427
sum	=	34.458247

atom contributions, total, positive, negative				
atom	1	0.146456	0.160089	-0.013633
atom	2	0.360759	0.602969	-0.242210
atom	3	1.660870	2.537700	-0.876830
atom	4	0.038509	0.348142	-0.309633
atom	5	0.189888	0.837074	-0.647186
atom	6	-0.065147	0.254184	-0.319331
atom	7	0.087350	0.223082	-0.135732
atom	8	0.134004	0.134837	-0.000833
atom	9	12.400467	13.201703	-0.801236
atom	10	18.795804	21.182930	-2.387125
atom	11	-0.099855	0.001160	-0.101015
atom	12	0.348248	0.589833	-0.241585
atom	13	-0.226098	0.043455	-0.269553
atom	14	-0.181982	0.048275	-0.230257
atom	15	-0.070422	0.340127	-0.410550
atom	16	-0.246021	0.043190	-0.289211
atom	17	-0.316793	0.045104	-0.361898
atom	18	2.697223	3.483665	-0.786441
atom	19	-0.371951	0.045484	-0.417435
atom	20	-0.249110	0.045557	-0.294667
atom	21	-0.069557	0.298798	-0.368355
atom	22	-0.069164	0.050876	-0.120039
atom	23	-0.090503	0.052504	-0.143007
atom	24	0.155788	0.877841	-0.722053
atom	25	-0.056245	0.061463	-0.117707
atom	26	-0.096751	0.046199	-0.142950
atom	27	0.131865	0.132722	-0.000857
atom	28	0.042600	0.042661	-0.000061
atom	29	0.030899	0.034738	-0.003838
atom	30	0.060629	0.214022	-0.153393
atom	31	0.035073	0.038036	-0.002963
atom	32	0.039115	0.039261	-0.000146
atom	33	-0.265259	0.070883	-0.336142
atom	34	-0.297923	0.022459	-0.320382
atom	35	-0.335949	0.061297	-0.397246
atom	36	0.060074	0.064009	-0.003936
atom	37	0.040599	0.041027	-0.000429
atom	38	0.055638	0.060718	-0.005080
atom	39	-0.106860	0.000934	-0.107794
atom	40	0.161976	0.172664	-0.010688

### S2.2.3 $\beta$ hydrogen (atom 30)

$$\sigma_{xx} = 27.345961$$

$$\sigma_{yy} = 24.952303$$

$$\sigma_{zz} = 40.364972$$

```

shielding constant   =      30.887746
positive contribution =      41.167843
negative contribution =     -10.280097
sum                  =      30.887746

```

```

atom contributions, total, positive, negative
atom   1      0.004496      0.041094     -0.036598
atom   2     -0.063361      0.175067     -0.238428
atom   3     -0.148612      0.235932     -0.384543
atom   4     -0.107577      0.118772     -0.226348
atom   5     -0.003176      0.178986     -0.182162
atom   6     -0.066798      0.090263     -0.157061
atom   7      0.021901      0.057046     -0.035144
atom   8      0.063094      0.063260     -0.000167
atom   9      1.234497      1.586524     -0.352027
atom  10      0.018819      0.193722     -0.174903
atom  11     -0.050825      0.010052     -0.060877
atom  12      0.913646      1.109601     -0.195955
atom  13     -0.158354      0.072990     -0.231344
atom  14     -0.150041      0.032926     -0.182967
atom  15      0.604652      0.860761     -0.256109
atom  16     -0.170582      0.060071     -0.230653
atom  17     -0.237858      0.028780     -0.266637
atom  18      2.938265      3.360239     -0.421973
atom  19     -0.314575      0.066323     -0.380899
atom  20     -0.222285      0.029549     -0.251834
atom  21      1.246181      1.963408     -0.717227
atom  22     -0.064628      0.056871     -0.121499
atom  23     -0.075842      0.035797     -0.111639
atom  24      7.059350      8.868898     -1.809549
atom  25     -0.037547      0.081577     -0.119124
atom  26     -0.077615      0.033987     -0.111602
atom  27      0.324435      0.354534     -0.030098
atom  28      0.045874      0.045936     -0.000062
atom  29      0.026897      0.028023     -0.001126
atom  30     18.482871     20.552587     -2.069715
atom  31      0.027967      0.038441     -0.010474
atom  32      0.029352      0.029630     -0.000277
atom  33      0.043812      0.263928     -0.220116
atom  34     -0.257156      0.020671     -0.277827
atom  35     -0.264196      0.029274     -0.293470
atom  36      0.057806      0.081596     -0.023790
atom  37      0.035448      0.036011     -0.000563
atom  38      0.038199      0.039588     -0.001389
atom  39     -0.093507      0.000142     -0.093649
atom  40      0.234717      0.234988     -0.000271

```

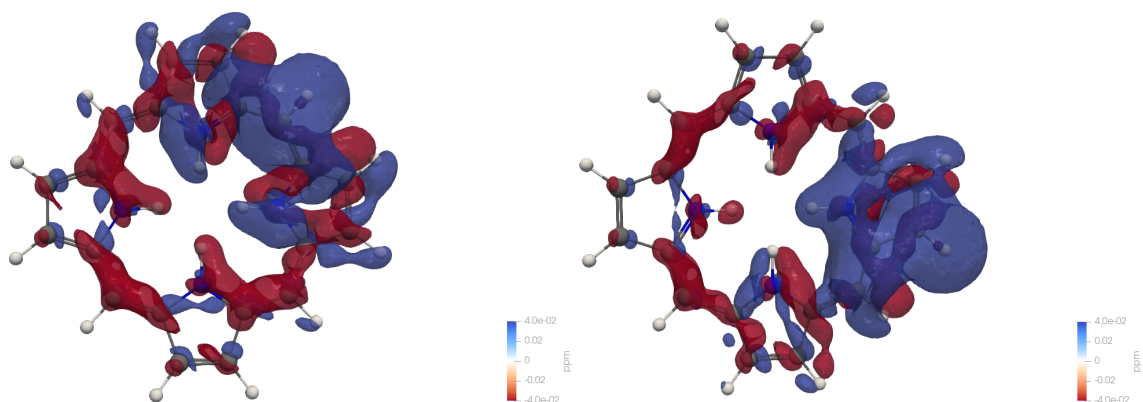


Figure S2: The isotropic  $^1\text{H}$  NMR shielding density of the *meso* and  $\beta$  hydrogens of free-base isophlorin. The shielding contributions are shown in blue and the deshielding contributions in red. An isovalue of  $\pm 0.04$  has been used.

## S2.3 Free-base trans-norcorrole

### S2.3.1 Inner hydrogen (atom 33)

$$\begin{aligned}\sigma_{xx} &= 18.815850 \\ \sigma_{yy} &= 26.894780 \\ \sigma_{zz} &= -71.887386\end{aligned}$$

```
shielding constant    =      -8.725585
positive contribution =      28.479121
negative contribution =     -37.204707
sum                   =     -8.725585
```

```
atom contributions, total, positive, negative
atom   1   -0.738810    0.116265   -0.855075
atom   2   -0.563592    0.267407   -0.830999
atom   3    0.021174    0.292900   -0.271726
atom   4   -0.084085    0.259506   -0.343591
atom   5   -1.876436    0.359555   -2.235991
atom   6   -1.408699    0.801953   -2.210652
atom   7   -0.085229    0.490310   -0.575539
atom   8   -0.082559    0.504351   -0.586911
atom   9   -1.587115    0.784564   -2.371680
atom  10   -2.040686    0.290199   -2.330885
atom  11   -1.987303    0.355541   -2.342845
atom  12   -0.007051    0.356095   -0.363146
atom  13   -0.038579    0.303527   -0.342107
atom  14   -0.737029    0.480049   -1.217077
atom  15   -1.085086    0.204193   -1.289279
atom  16   -0.045413    0.213404   -0.258817
atom  17   -0.045016    0.206217   -0.251233
atom  18   -0.627011    0.184123   -0.811134
atom  19    0.117178    0.117852   -0.000674
atom  20    0.244632    0.246063   -0.001431
atom  21    0.125937    0.126228   -0.000291
atom  22    0.134168    0.136976   -0.002808
atom  23    0.219467    0.219792   -0.000325
atom  24    0.217167    0.217655   -0.000488
atom  25    0.151871    0.152982   -0.001111
atom  26    0.150495    0.150785   -0.000290
```

atom	27	0.110497	0.111269	-0.000772
atom	28	0.106603	0.106801	-0.000199
atom	29	-2.189189	0.585587	-2.774776
atom	30	-0.779130	3.878476	-4.657606
atom	31	-3.050425	1.204457	-4.254882
atom	32	-1.014981	0.251435	-1.266416
atom	33	10.275801	14.480523	-4.204722
atom	34	-0.527149	0.022080	-0.549229

### S2.3.2 Meso hydrogen (atom 20)

$$\sigma_{xx} = 24.008456$$

$$\sigma_{yy} = 28.565149$$

$$\sigma_{zz} = 34.981831$$

shielding constant	=	29.185145
positive contribution	=	40.299796
negative contribution	=	-11.114650
sum	=	29.185145

atom contributions, total, positive, negative				
atom	1	-0.229709	0.035477	-0.265187
atom	2	-0.163659	0.066966	-0.230625
atom	3	0.015107	0.103553	-0.088445
atom	4	-0.046697	0.087293	-0.133990
atom	5	-0.360473	0.067913	-0.428385
atom	6	0.055281	0.337064	-0.281783
atom	7	0.070690	0.314917	-0.244227
atom	8	0.079296	0.680340	-0.601044
atom	9	0.724202	1.715256	-0.991055
atom	10	8.932376	10.218120	-1.285745
atom	11	1.056566	2.034835	-0.978269
atom	12	-0.050762	0.655156	-0.705918
atom	13	0.194003	0.405308	-0.211305
atom	14	0.160146	0.423316	-0.263170
atom	15	-0.335328	0.067046	-0.402373
atom	16	-0.030570	0.097180	-0.127750
atom	17	-0.017577	0.089139	-0.106716
atom	18	-0.160243	0.068042	-0.228285
atom	19	0.041792	0.042278	-0.000486
atom	20	18.562535	20.491083	-1.928548
atom	21	0.049347	0.049448	-0.000101
atom	22	0.034807	0.042623	-0.007816
atom	23	0.134429	0.134892	-0.000462
atom	24	0.106552	0.202215	-0.095663
atom	25	0.089948	0.202073	-0.112125
atom	26	0.140968	0.141322	-0.000354
atom	27	0.036742	0.044504	-0.007762
atom	28	0.050087	0.050165	-0.000077
atom	29	-0.307741	0.081796	-0.389536
atom	30	0.258535	0.553010	-0.294474
atom	31	0.262145	0.601925	-0.339780
atom	32	-0.204050	0.078085	-0.282136
atom	33	0.088347	0.109438	-0.021091
atom	34	-0.051949	0.008019	-0.059968

### S2.3.3 $\beta$ hydrogen at pyrrole with inner hydrogen (atom 23)

$$\sigma_{xx} = 27.091696$$

$$\sigma_{yy} = 25.961988$$

$$\sigma_{zz} = 31.426613$$

shielding constant	=	28.160099
positive contribution	=	38.864468
negative contribution	=	-10.704368
sum	=	28.160099

atom contributions, total, positive, negative				
atom	1	-0.178707	0.063806	-0.242513
atom	2	0.072004	0.252699	-0.180694
atom	3	0.133557	0.290359	-0.156802
atom	4	-0.137074	0.349481	-0.486554
atom	5	0.186813	0.762382	-0.575569
atom	6	2.658028	3.126237	-0.468209
atom	7	5.161418	7.215018	-2.053600
atom	8	0.955871	1.631803	-0.675932
atom	9	0.713009	0.951154	-0.238145
atom	10	-0.155876	0.182011	-0.337887
atom	11	-0.341734	0.066825	-0.408558
atom	12	-0.018903	0.098755	-0.117658
atom	13	-0.000350	0.093451	-0.093801
atom	14	-0.159936	0.083876	-0.243812
atom	15	-0.231651	0.045709	-0.277361
atom	16	-0.027209	0.069539	-0.096748
atom	17	-0.026410	0.071500	-0.097909
atom	18	-0.245072	0.043828	-0.288900
atom	19	0.045775	0.048396	-0.002621
atom	20	0.057046	0.075961	-0.018915
atom	21	0.095304	0.096643	-0.001340
atom	22	-0.043690	0.101631	-0.145322
atom	23	18.457445	20.713215	-2.255771
atom	24	0.321424	0.353751	-0.032327
atom	25	0.037211	0.042843	-0.005632
atom	26	0.050422	0.050493	-0.000071
atom	27	0.039792	0.040058	-0.000266
atom	28	0.037675	0.038374	-0.000698
atom	29	0.190379	0.411106	-0.220726
atom	30	0.953497	1.184922	-0.231425
atom	31	-0.317597	0.095770	-0.413367
atom	32	-0.211959	0.048697	-0.260656
atom	33	0.153636	0.158537	-0.004901
atom	34	-0.064038	0.005636	-0.069674

### S2.3.4 $\beta$ hydrogen at pyrrole without inner hydrogen (atom 21)

$$\sigma_{xx} = 22.832178$$

$$\sigma_{yy} = 26.561766$$

$$\sigma_{zz} = 31.283136$$

shielding constant	=	26.892360
positive contribution	=	37.531359
negative contribution	=	-10.638998
sum	=	26.892360

atom contributions, total, positive, negative				
atom	1	0.682547	1.097700	-0.415152
atom	2	2.237483	2.701635	-0.464152
atom	3	3.738517	6.579535	-2.841018
atom	4	1.251080	1.851137	-0.600058
atom	5	0.832816	1.075474	-0.242657
atom	6	-0.202722	0.147203	-0.349924
atom	7	-0.026768	0.144013	-0.170781
atom	8	0.000824	0.112207	-0.111382
atom	9	-0.071289	0.103694	-0.174983
atom	10	-0.205351	0.034365	-0.239716
atom	11	-0.189847	0.042074	-0.231921
atom	12	0.001127	0.073099	-0.071972
atom	13	-0.027527	0.061396	-0.088922
atom	14	-0.251108	0.045826	-0.296934
atom	15	-0.110055	0.113689	-0.223744
atom	16	-0.007889	0.120534	-0.128423
atom	17	-0.021424	0.159819	-0.181243
atom	18	-0.291123	0.141751	-0.432874
atom	19	0.038702	0.173506	-0.134804
atom	20	0.037441	0.038253	-0.000812
atom	21	18.237133	20.214435	-1.977302
atom	22	0.351699	0.376998	-0.025298
atom	23	0.017970	0.049141	-0.031171
atom	24	0.057390	0.057588	-0.000198
atom	25	0.037123	0.037258	-0.000135
atom	26	0.032463	0.034345	-0.001882
atom	27	0.065270	0.065361	-0.000091
atom	28	0.037381	0.058575	-0.021194
atom	29	1.155757	1.417526	-0.261769
atom	30	-0.081019	0.136518	-0.217537
atom	31	-0.284765	0.058228	-0.342993
atom	32	-0.128939	0.154254	-0.283193
atom	33	-0.006313	0.023623	-0.029936
atom	34	-0.014225	0.030601	-0.044826

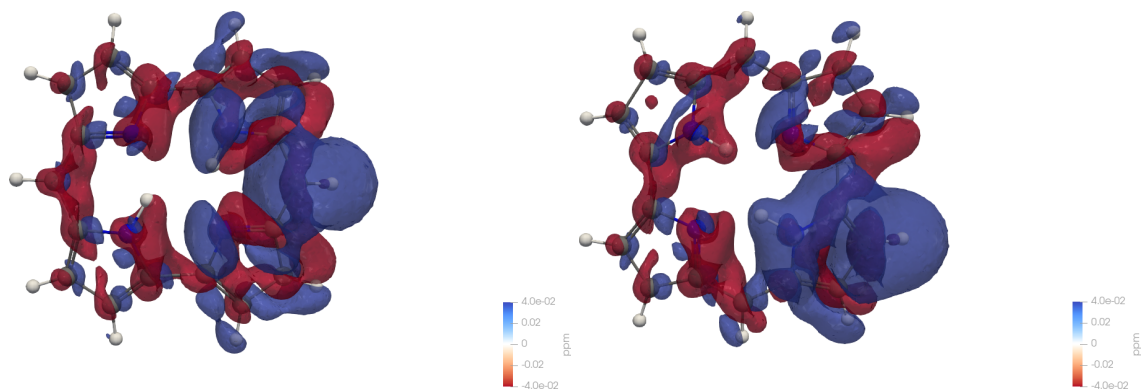


Figure S3: The isotropic  $^1\text{H}$  NMR shielding density of the *meso* and  $\beta$  hydrogens of free-base *trans*-norcorrole. The shielding contributions are shown in blue and the deshielding contributions in red. An isovalue of  $\pm 0.04$  has been used.