Supporting Information

Activation of Hydrocarbon C-H Bonds by Iodosylbenzene. How Does It Compare with Iron(IV)-Oxo Oxidants?

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Experimental Section

All chemicals obtained from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use.[1] Iodosylbenzene (PhIO) was prepared by a literature method.[2] The deuterated substrate 9,10-dihydroanthracene-d_4, was prepared by taking 9,10-dihydroanthracene (0.5 g, 2.7 mmol) in DMSO-d_6 (3 mL) along with NaH (0.2 g, 8.1 mmol) under an inert atmosphere.[3] After the deep red solution was stirred at room temp for 8 h, the reaction was quenched with D_2O (5 mL). The crude product was filtered and washed with copious amounts of H_2O. ^1H NMR confirmed >99% deuteration.

All reactions were carried out under inert atmosphere. Solid PhIO (0.16 mmol) was added to a reaction solution containing 1,4-cyclohexadiene (0.40 mmol) in CH_3CN (2 mL) at 25 ^oC. After the reaction solution was stirred for 30 min and filtered through 0.45 ⌈M filter, the reaction mixture was analyzed with Agilent Technologies 6890N gas chromatography equipped with a FID detector. To determine the KIE value, a competitive reaction was carried out by adding PhIO (0.02 mmol) to a reaction solution containing DHA (0.1 mmol) and DHA-d_4 (0.1 mmol) in CH_3CN (2 mL) at 25 ^oC. After 30 min stirring, the reaction mixture

was directly analyzed with Thermo Finnigan Focus DSQ mass spectrometer interfaced with Focus gas chromatography. The product ratio of anthracene (AN) and anthracene-d_2 (AN-d_2) was determined from the relative abundances of the mass peaks at m/z = 178 for AN and at m/z = 180 for AN-d_2.

All calculations were performed using established procedures in the field.[4] We employed the UB3LYP hybrid density functional method as implemented in Gaussian-03.[5,6] Geometry optimizations followed by a frequency calculation were performed with a LANL2DZ basis set on iodine that includes a core potential and a 6–31G basis set on the rest of the atoms (basis set B1).[7] Subsequent single point calculations were performed in Jaguar 7.0 using the LACV3P+ basis set on iodine and 6–311+G* on the rest of the atoms (basis set B2) and confirmed the energetics.[8] All structures were fully optimized (without constraints) and a subsequent frequency calculated confirmed them as local minima or transition state structures. Intrinsic reaction coordinate (IRC) calculations starting from the optimized transition state structure confirmed that it connects to reactants and products directly.

Kinetic isotope effect calculations using the Eyring (KIE_E) or Wigner tunneling (KIE_W) model were used using data obtained from the Gaussian frequency calculations. Various hydrogen atoms were replaced by deuterium atoms. The Eyring kinetic isotope effect was estimated from the relative free energies of activation ($\Delta G^{\ddagger}$) relative to the reactant complex for the hydrogen and deuterium substituted systems using $KIE_E = \exp((\Delta G_D^{\ddagger} - \Delta G_H^{\ddagger})/RT)$ with R the gas constant and T the estimated temperature (298.15 K). Subsequent calculation of KIE_W was done by multiplying KIE_E with the tunneling ratio Q_{tH}/Q_{tD} with $Q_t = 1 + {}^1/_{24}(h\nu/kT)^2$, with h Planck's constant, ν the imaginary frequency in the transition state, k the Boltzmann constant and T the temperature.[9,10]

References

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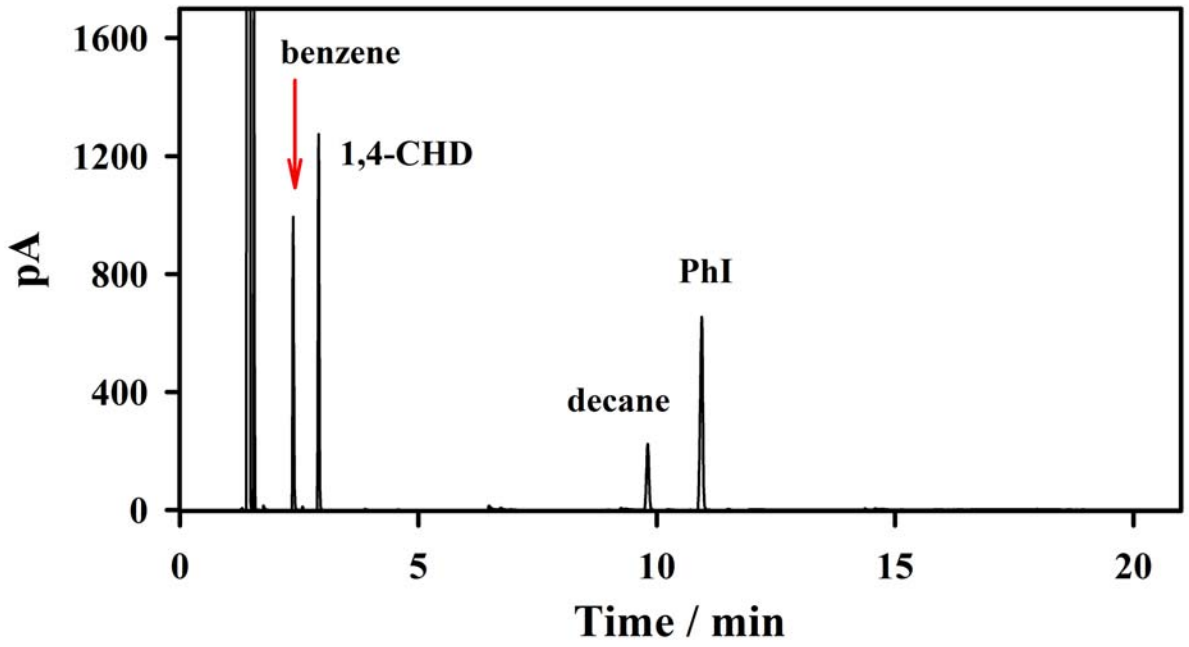


Figure S1. Gas chromatogram showing the product analysis of a reaction solution carried out with 1,4-cyclohexadiene (1,4-CHD; 0.40 mmol) and PhIO (0.16 mmol) in CH_3CN (2 mL) for 30 min at 25 ^{o}C. *n*-Decane (0.04 mmol) was used as an internal standard. Benzene, as a sole product, was produced in high yield, which is 85 % based on PhIO added.

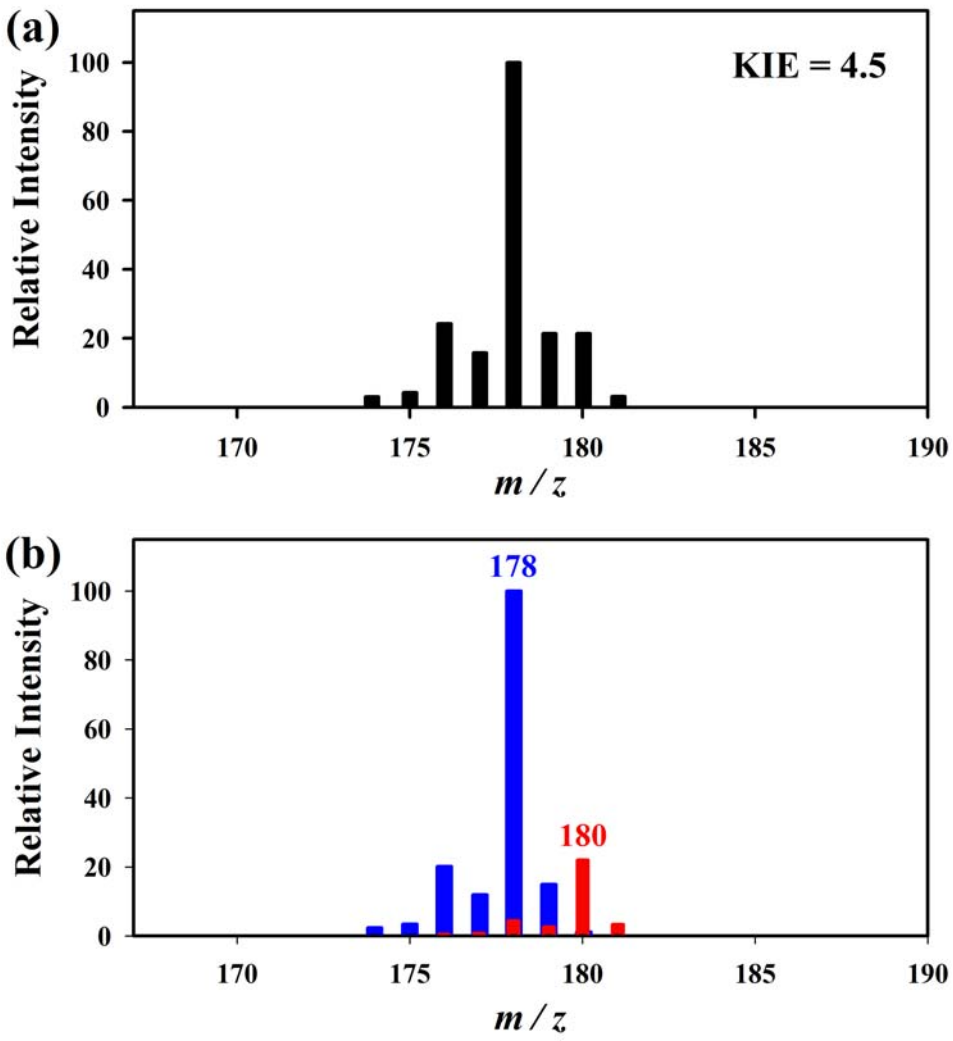


Figure S2. (a) GC-MS spectrum of products formed in the reaction of solid PhIO (0.02 mmol) with a mixture of 9,10-dihydroanthracene (1.0 mmol) and 9,10-dihydroanthracene-d_4 (0.1 mmol) in CH_3CN (2 mL) at 25 ^oC. (b) Simulated GC-MS spectrum of anthracene (blue) and anthracene-d_2 (red). The product ratio of anthracene and anthracene-d_2 in (a) was calculated to be1.00:0.22, indicating KIE value of 4.5.

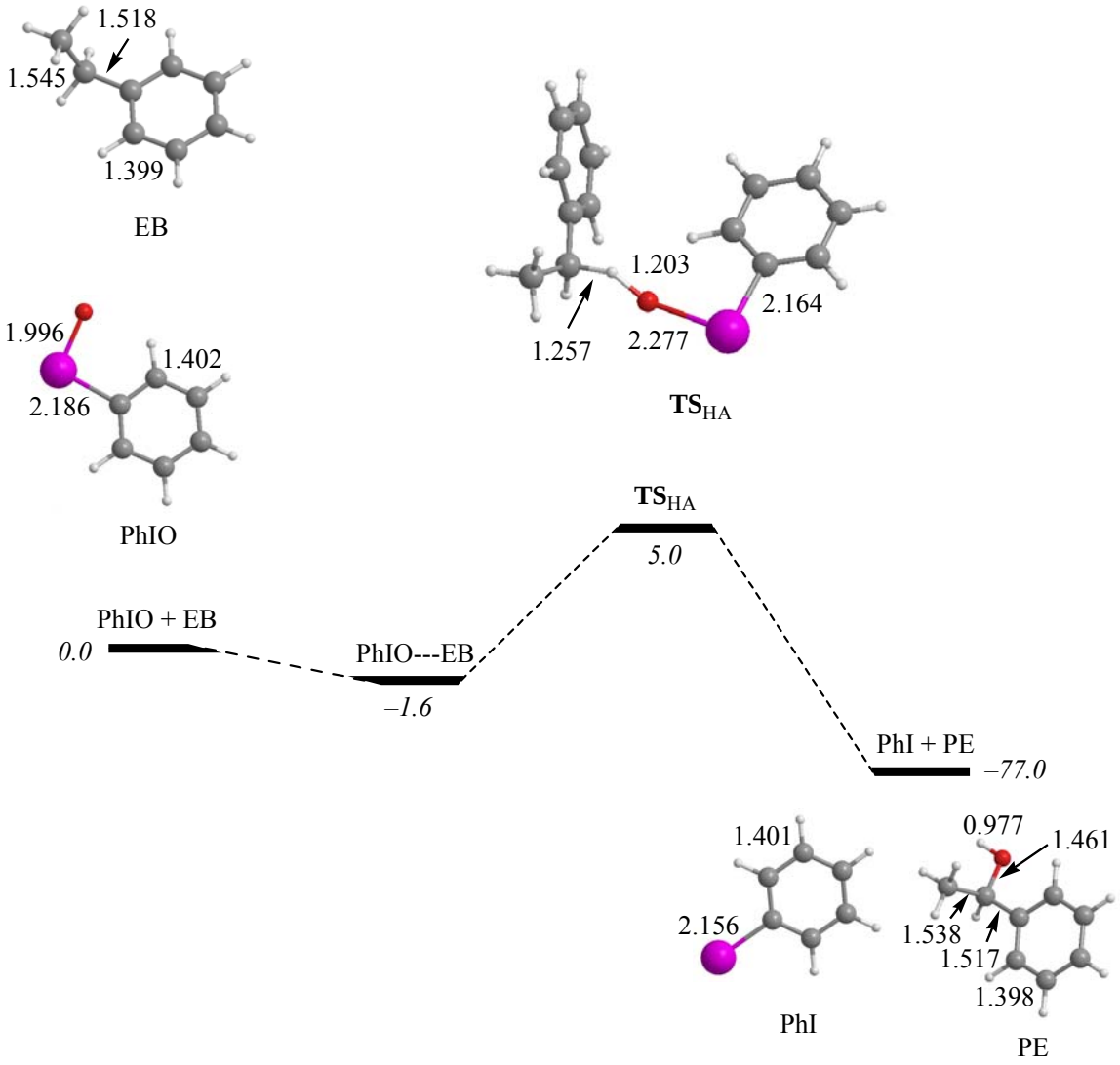
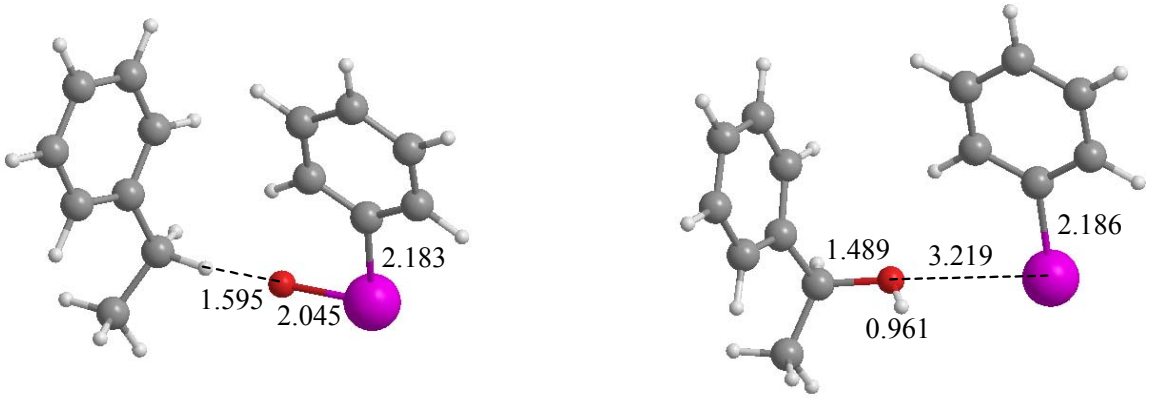


Fig. S3 Potential energy profile (B3LYP/B2//B3LYP/B1 with ZPE/B1) for the reaction of iodosylbenzene (PhIO) with ethylbenzene (EB) leading to iodobenzene (PhI) and 1-phenylethanol (PE) via a hydrogen abstraction transition state (**TS**$_{HA}$). Also shown are optimized geometries along the reaction mechanism with bond lengths in Ångstroms. Energies reported in italics are in kcal mol^{-1}.



Forward Scan **Reverse Scan**

Fig. S4 Optimized geometries of structures of the last point of the IRCs: (a) Forward scan. (b) Reverse Scan.

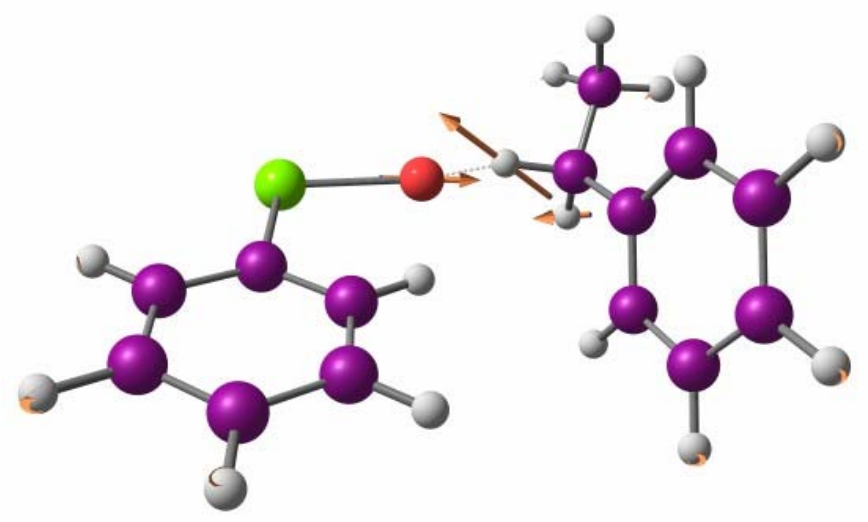
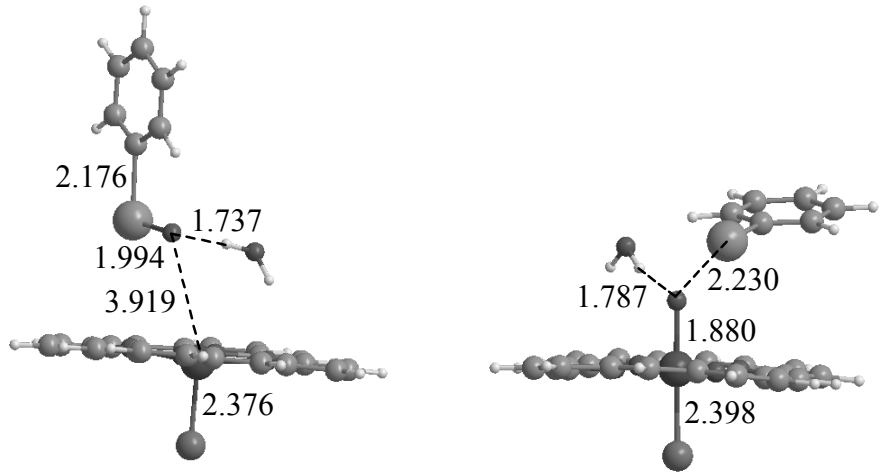


Fig. S5 Vector of the imaginary mode (*i*426.4 cm^{-1}) in the transition state.



*i*24.7 cm^{-1} *i*374.0 cm^{-1}

TS0 **TS1**

Fig. S6 Optimized geometries of **TS0** and **TS1** as obtained with UB3LYP/B1 in Gaussian-03.

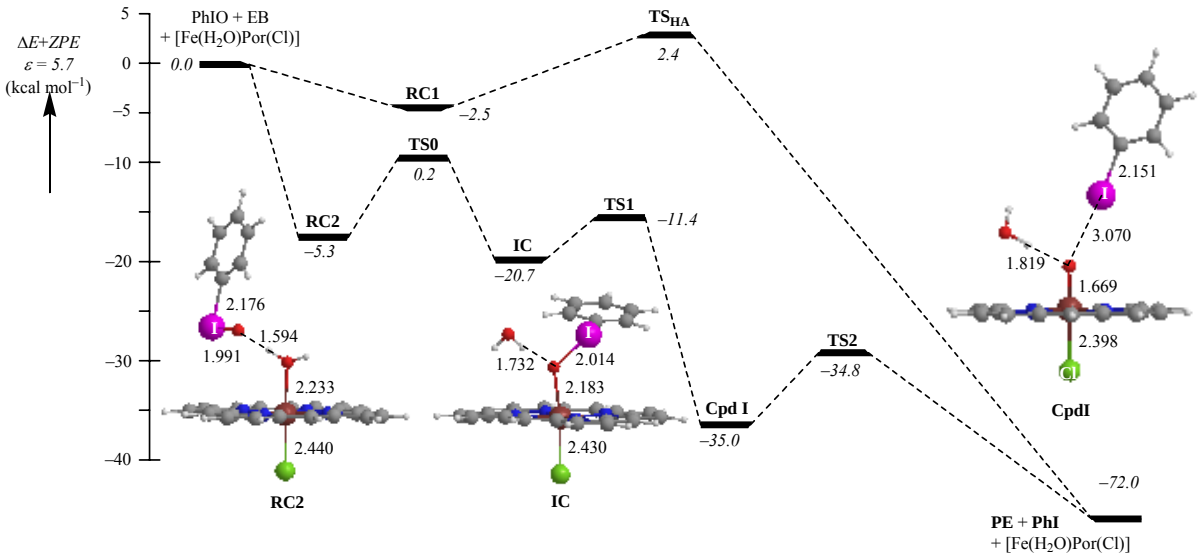


Fig. S7 Potential energy profile in a dielectric constant of $\varepsilon = 5.7$.

Table S1. Group spin densities and charges for the reaction of Fe(Por)Cl(H_2O) with PhIO to form Compound I and PhI. Data obtained from UB3LYP/B2 calculations in Jaguar.

Spin Densities	ρ_{Fe}	ρ_{Por}	ρ_{Cl}	ρ_{H2O}	ρ_{PhIO}	ρ_{O}
Fe(Por)Cl(H_2O)	2.93	-0.16	0.23	0.00		
Fe(Por)Cl(H_2O)--PhIO	2.93	-0.15	0.20	0.02	0.00	
TS0	2.89	-0.18	0.28	0.01	0.00	
Fe(Por)Cl(PhIO)--H_2O	2.83	-0.11	0.24	0.00	0.05	
TS1	2.36	-0.09	0.19	0.00	0.29	0.25
CpdI--PhI--H_2O	1.25	0.86	0.11	0.01	0.00	0.78
CpdI--H_2O	1.19	0.84	0.13	0.01		0.83
Charges	Q_{Fe}	Q_{Por}	Q_{Cl}	Q_{H2O}	Q_{PhIO}	Q_{O}
Fe(Por)Cl(H_2O)	0.34	-0.10	-0.37	0.14		
Fe(Por)Cl(H_2O)--PhIO	0.29	-0.07	-0.43	0.17	0.04	
TS0	0.10	0.19	-0.41	0.11	0.01	
Fe(Por)Cl(PhIO)--H_2O	0.33	-0.08	-0.40	0.12	0.04	
TS1	0.37	0.03	-0.42	0.11	0.48	-0.56
CpdI--PhI--H_2O	0.17	0.60	-0.43	0.04	0.01	-0.40
CpdI--H_2O	0.21	0.52	-0.44	0.03		-0.32

Table S2. Kinetic isotope effect calculations for the replacement of one or more hydrogen atoms of ethylbenzene (EB) by deuterium atoms in the reaction of PhIO with ethylbenzene.

[a]	Imag. Freq [b]	ΔG [c]	KIE(E) [d]	KIE(W) [e]
EB-h_{10}	426.4	6.86		
EB-d_{10}	399.4	7.59	3.41	3.78
$C_6D_5CH_2CH_3$	426.2	6.86	1.00	1.00
$C_6H_5CH_2CD_3$	425.6	6.85	0.99	0.99
EB:benzyl-d_1	402.1	7.62	3.63	3.98
$C_6H_5CD_2CH_3$	400.2	7.60	3.47	3.84
EB:secondary benzyl-d_1	423.3	6.83	0.95	0.96

a) Ethylbenzene with levels of deuteration mentioned; benzyl-d_1 refers to the transferrable hydrogen atom replaced by deuterium, in secondary benzyl-d_1 not the transferable hydrogen atom but the other is replaced by deuterium.

b) Imaginary frequency of the transition state (in cm^{-1}).

c) Free energy (UB3LYP/B1) in kcal mol^{-1}.

d) Kinetic isotope effect from Eyring equation: $KIE(E) = \exp((-\Delta G_H + \Delta G_D)/RT)$

e) Kinetic isotope effect from Wigner equation: $KIE(W) = KIE(E) * Q_{tH}/Q_{tD}$ with $Q_t = 1 + {}^1/_{24}(h\nu/kT)^2$

Cartesian coordinates of optimized geometries:

^{4}Fe(Por)Cl(H_2O):

Fe1	0.0077380000	0.0116880000	0.0153640000
N2	-0.6374330000	1.9154150000	-0.1043000000
N3	1.9143870000	0.6464730000	-0.1496130000
N4	-1.9070870000	-0.6352880000	-0.1582280000
N5	0.6490970000	-1.9040050000	-0.1268830000
C6	-1.9541280000	2.3506060000	-0.0888990000
C7	3.0597720000	-0.1398000000	-0.1175150000
C8	0.1484850000	3.0571140000	-0.1192540000
C9	2.3500440000	1.9650620000	-0.1452890000
C10	-3.0526880000	0.1514820000	-0.1157110000
C11	1.9673230000	-2.3422710000	-0.0934200000
C12	-2.3441370000	-1.9564060000	-0.1288100000
C13	-0.1393720000	-3.0484180000	-0.1122110000
C14	-1.9903400000	3.7966730000	-0.0880680000
C15	4.2312700000	0.7062230000	-0.1113330000
C16	-0.6957100000	4.2317330000	-0.1082060000
C17	3.7943270000	2.0014340000	-0.1289550000
C18	-4.2230900000	-0.6937920000	-0.0875190000
C19	2.0008530000	-3.7862530000	-0.0685220000
C20	-3.7873140000	-1.9904320000	-0.0963380000
C21	0.7045120000	-4.2209210000	-0.0808700000
H22	-2.8952750000	4.3863930000	-0.0738430000
H23	5.2485240000	0.3434190000	-0.0879280000
H24	-0.3304870000	5.2482950000	-0.1129550000
H25	4.3838460000	2.9066110000	-0.1229400000
H26	-5.2400130000	-0.3307520000	-0.0555010000
H27	2.9044690000	-4.3775550000	-0.0391200000
H28	-4.3782420000	-2.8944670000	-0.0722590000
H29	0.3397320000	-5.2376020000	-0.0629750000
C30	-3.0766750000	1.5373610000	-0.0908320000
C31	3.0880820000	-1.5257040000	-0.0923520000
C32	-1.5259520000	-3.0759770000	-0.1189130000
C33	1.5339000000	3.0851830000	-0.1396710000
H34	-4.0467100000	2.0215200000	-0.0642030000
H35	4.0594570000	-2.0069610000	-0.0617540000
H36	-2.0071940000	-4.0476480000	-0.0966210000
H37	2.0158600000	4.0566710000	-0.1400720000
O38	-0.0870300000	-0.0194460000	-2.3385240000
H39	-0.8965210000	-0.5259890000	-2.5409770000
H40	0.6883440000	-0.4203140000	-2.7732800000
Cl41	-0.0010860000	-0.0026740000	2.4224980000

^{4}Fe(Por)Cl(H_2O)—PhIO:

Fe1	1.8520970000	0.0547490000	-0.2162220000
N2	1.7819270000	2.0497070000	-0.5183110000
N3	0.5432510000	-0.2232220000	-1.7320250000
N4	2.9998580000	0.3530420000	1.4306070000
N5	1.8212120000	-1.9295440000	0.1690420000
C6	2.4547430000	3.0225250000	0.2009830000
C7	0.0789690000	-1.4406920000	-2.2128260000
C8	1.1035100000	2.7096630000	-1.5299370000
C9	0.0574450000	0.7509830000	-2.5912060000
C10	3.5252950000	1.5610780000	1.8669520000
C11	1.1710820000	-2.9081620000	-0.5661040000
C12	3.5437550000	-0.6283860000	2.2480630000
C13	2.5134660000	-2.5891640000	1.1714390000
C14	2.1905470000	4.3248790000	-0.3745380000
C15	-0.7374140000	-1.2173070000	-3.3855430000

C16	1.3587260000	4.1322520000	-1.4402940000
C17	-0.7484260000	0.1335520000	-3.6187190000
C18	4.3985720000	1.3310170000	2.9966490000
C19	1.4634930000	-4.2113780000	-0.0085490000
C20	4.4095310000	-0.0158520000	3.2314720000
C21	2.2889310000	-4.0151260000	1.0616320000
H22	2.5994410000	5.2531020000	-0.0026210000
H23	-1.2068600000	-2.0000260000	-3.9645080000
H24	0.9516760000	4.8716420000	-2.1147010000
H25	-1.2344880000	0.6689940000	-4.4218000000
H26	4.9344920000	2.1063420000	3.5247080000
H27	1.0805470000	-5.1438210000	-0.3969610000
H28	4.9562560000	-0.5583450000	3.9890820000
H29	2.7171820000	-4.7551380000	1.7219290000
C30	3.2654850000	2.8020280000	1.3052440000
C31	0.3631170000	-2.6873380000	-1.6697950000
C32	3.3105540000	-1.9910720000	2.1372450000
C33	0.3052560000	2.1136130000	-2.4929950000
H34	3.7418120000	3.6656340000	1.7564730000
H35	-0.0721250000	-3.5552540000	-2.1533760000
H36	3.8018640000	-2.6420370000	2.8522360000
H37	-0.1480640000	2.7594410000	-3.2374240000
O38	-1.9278720000	-1.3087990000	1.0255500000
C39	-5.4351010000	0.5144310000	2.9870530000
C40	-6.4834730000	1.2886770000	2.4748430000
C41	-6.5679400000	1.5422680000	1.1003040000
C42	-5.6032030000	1.0225770000	0.2248000000
C43	-4.5780190000	0.2559730000	0.7706260000
C44	-4.4624360000	-0.0149750000	2.1275460000
H45	-5.3695030000	0.3193490000	4.0523230000
H46	-7.2331610000	1.6957160000	3.1449900000
H47	-7.3780930000	2.1451200000	0.7034760000
H48	-5.6655770000	1.2243470000	-0.8395060000
I49	-3.0219920000	-0.6067220000	-0.4825530000
H50	-3.6321590000	-0.6171270000	2.4866200000
O51	0.1400770000	0.2765080000	1.1998410000
H52	0.4846570000	0.3562670000	2.1061020000
H53	-0.6610050000	-0.3497040000	1.1530690000
Cl54	3.7943530000	-0.1717450000	-1.6763180000

^{4}Fe(Por)Cl(PhIO)—H_2O:

Fe1	1.1749060000	0.1160420000	0.6499690000
N2	2.3313310000	1.3521480000	-0.4399640000
N3	2.1943100000	-1.4830720000	-0.0578930000
N4	0.0561860000	1.6931550000	1.2313280000
N5	-0.1216570000	-1.1416630000	1.5624830000
C6	2.2830710000	2.7384560000	-0.4623000000
C7	1.9940660000	-2.8153720000	0.2709500000
C8	3.4092740000	0.9861350000	-1.2350960000
C9	3.2908920000	-1.4496810000	-0.9021270000
C10	0.3145450000	3.0317290000	0.9824150000
C11	0.0046740000	-2.5200220000	1.6869990000
C12	-1.0720470000	1.6575490000	2.0376100000
C13	-1.2155340000	-0.7809900000	2.3376120000
C14	3.3490950000	3.2493640000	-1.2954720000
C15	2.9906110000	-3.6338540000	-0.3851680000
C16	4.0387270000	2.1714360000	-1.7741180000
C17	3.7871530000	-2.7929020000	-1.1107150000
C18	-0.6746010000	3.8521350000	1.6481100000
C19	-1.0480850000	-3.0304710000	2.5343140000

C20	-1.5304240000	3.0055500000	2.2941370000
C21	-1.8019770000	-1.9600330000	2.9318170000
H22	3.5345240000	4.2976720000	-1.4786810000
H23	3.0607860000	-4.7078560000	-0.2913270000
H24	4.9013140000	2.1643020000	-2.4242920000
H25	4.6386700000	-3.0428170000	-1.7267800000
H26	-0.6949390000	4.9319560000	1.6194030000
H27	-1.1740010000	-4.0713650000	2.7953360000
H28	-2.3898750000	3.2554360000	2.8990610000
H29	-2.6638940000	-1.9536750000	3.5832660000
C30	1.3528170000	3.5229140000	0.2028620000
C31	0.9834000000	-3.2993360000	1.0878910000
C32	-1.6679500000	0.5142310000	2.5452680000
C33	3.8511210000	-0.3075390000	-1.4562450000
H34	1.4447060000	4.5996890000	0.1083950000
H35	0.9563420000	-4.3677120000	1.2732590000
H36	-2.5415420000	0.6432070000	3.1748350000
H37	4.7169440000	-0.4364310000	-2.0966360000
O38	0.1106110000	0.1423300000	-1.2562610000
C39	-4.6177750000	1.5959820000	-0.9086340000
C40	-5.5335980000	0.7973780000	-0.2131740000
C41	-5.2417990000	-0.5465610000	0.0497750000
C42	-4.0310780000	-1.1013580000	-0.3859460000
C43	-3.1553210000	-0.2835260000	-1.1021140000
C44	-3.4048400000	1.0620400000	-1.3691680000
H45	-4.8392470000	2.6408250000	-1.0995630000
H46	-6.4710940000	1.2224280000	0.1302890000
H47	-5.9432190000	-1.1633120000	0.6019660000
H48	-3.7855890000	-2.1322310000	-0.1574090000
I49	-1.3143490000	-1.1577370000	-1.8349230000
H50	-2.6732140000	1.6838840000	-1.8903020000
O51	-0.7986560000	2.4213860000	-2.4003110000
H52	-0.5295910000	3.1987330000	-1.8781210000
H53	-0.3124080000	1.6259430000	-2.0443780000
Cl54	2.6020570000	0.2659450000	2.6104370000

^{4}CpdI—PhI—H_2O:

Fe1	-1.7598370000	0.1640560000	0.2062450000
N2	-2.6602290000	-0.1210950000	-1.5798970000
N3	-1.5122000000	2.1211440000	-0.2366030000
N4	-2.1645960000	-1.7497750000	0.7102110000
N5	-1.0252330000	0.4925850000	2.0606170000
C6	-3.1666580000	-1.3058620000	-2.0754700000
C7	-0.9282210000	3.0854780000	0.5628330000
C8	-2.8505230000	0.8189580000	-2.5765270000
C9	-1.8531620000	2.7588630000	-1.4128760000
C10	-2.7298670000	-2.7177110000	-0.0942370000
C11	-0.5112380000	1.6777270000	2.5525390000
C12	-1.8774460000	-2.3737300000	1.9108360000
C13	-0.8986770000	-0.4286730000	3.0813100000
C14	-3.6890500000	-1.1066030000	-3.4094970000
C15	-0.9002820000	4.3558320000	-0.1293670000
C16	-3.4962400000	0.2087070000	-3.7189270000
C17	-1.4744000000	4.1540040000	-1.3519730000
C18	-2.8017020000	-3.9769770000	0.6146470000
C19	-0.0522370000	1.4945860000	3.9122770000
C20	-2.2765360000	-3.7638700000	1.8565530000
C21	-0.2938320000	0.1910260000	4.2403310000
H22	-4.1357720000	-1.8806400000	-4.0152130000
H23	-0.4981160000	5.2704490000	0.2805090000

H24	-3.7568130000	0.7297590000	-4.6281760000
H25	-1.6355060000	4.8699720000	-2.1442130000
H26	-3.2030100000	-4.8907450000	0.2025730000
H27	0.3894010000	2.2690730000	4.5216470000
H28	-2.1635620000	-4.4677740000	2.6676970000
H29	-0.0889750000	-0.3156900000	5.1717250000
C30	-3.1829220000	-2.5141380000	-1.3915240000
C31	-0.4574930000	2.8759010000	1.8525800000
C32	-1.2923450000	-1.7597860000	3.0088810000
C33	-2.4741760000	2.1523230000	-2.4983140000
H34	-3.5910660000	-3.3723710000	-1.9136250000
H35	-0.0232620000	3.7283680000	2.3648800000
H36	-1.1284810000	-2.3724060000	3.8894790000
H37	-2.6850430000	2.7772940000	-3.3600030000
O38	-0.2610610000	-0.2421720000	-0.4061950000
C39	7.0875060000	0.8964710000	-0.3644470000
C40	7.7546140000	-0.3256920000	-0.5036770000
C41	7.0166370000	-1.5104230000	-0.6025370000
C42	5.6165020000	-1.4778850000	-0.5631560000
C43	4.9578420000	-0.2512700000	-0.4237240000
C44	5.6877150000	0.9384560000	-0.3237620000
H45	7.6516490000	1.8208960000	-0.2876780000
H46	8.8389930000	-0.3545450000	-0.5353440000
H47	7.5254010000	-2.4632930000	-0.7114030000
H48	5.0502750000	-2.3990510000	-0.6400310000
I49	2.8086520000	-0.1908970000	-0.3684200000
H50	5.1758390000	1.8881000000	-0.2177800000
O51	-0.0981640000	-2.4040230000	-2.1777960000
H52	0.8289010000	-2.7042590000	-2.1467930000
H53	-0.1695460000	-1.5887220000	-1.6252630000
Cl54	-3.9151380000	0.7472320000	1.0803480000

^{4}CpdI—H_2O:

Fe1	0.0979160000	-0.0003100000	0.0801700000
N2	-1.2600610000	-1.4790820000	-0.1338190000
N3	1.5818350000	-1.3742600000	0.1160300000
N4	-1.3667210000	1.3723190000	-0.1409900000
N5	1.4752730000	1.4811130000	0.1104770000
C6	-2.6282750000	-1.3396090000	-0.2556620000
C7	2.9381920000	-1.1310170000	0.2244210000
C8	-1.0164370000	-2.8405140000	-0.1342380000
C9	1.4447060000	-2.7475580000	0.0806460000
C10	-2.7195600000	1.1303400000	-0.2615880000
C11	2.8454840000	1.3399240000	0.2196120000
C12	-1.2243490000	2.7486640000	-0.1522880000
C13	1.2367190000	2.8407900000	0.0651540000
C14	-3.2579920000	-2.6399140000	-0.3357160000
C15	3.6673710000	-2.3809640000	0.2579830000
C16	-2.2609330000	-3.5688440000	-0.2619440000
C17	2.7427730000	-3.3817380000	0.1693320000
C18	-3.4445730000	2.3791890000	-0.3524300000
C19	3.4801430000	2.6401730000	0.2458970000
C20	-2.5191890000	3.3811900000	-0.2862970000
C21	2.4840960000	3.5695080000	0.1492490000
H22	-4.3211170000	-2.8019090000	-0.4316760000
H23	4.7413800000	-2.4644150000	0.3344580000
H24	-2.3428350000	-4.6452670000	-0.2888030000
H25	2.9076200000	-4.4489600000	0.1590090000
H26	-4.5163370000	2.4607190000	-0.4560170000
H27	4.5450220000	2.8032420000	0.3217160000

H28	-2.6807940000	4.4482440000	-0.3270820000
H29	2.5701710000	4.6458740000	0.1303990000
C30	-3.3052790000	-0.1288050000	-0.3020440000
C31	3.5212300000	0.1277650000	0.2804090000
C32	-0.0177630000	3.4270790000	-0.0533400000
C33	0.2371710000	-3.4265490000	-0.0314260000
H34	-4.3859750000	-0.1695020000	-0.3830210000
H35	4.6024300000	0.1685120000	0.3646850000
H36	-0.0564420000	4.5113910000	-0.0774420000
H37	0.2789900000	-4.5108260000	-0.0454760000
O38	-0.0563230000	-0.0103260000	1.7386260000
O39	-2.6081910000	-0.0746590000	2.8650640000
H40	-2.6269000000	0.7748300000	3.3437500000
H41	-1.6831640000	-0.2154230000	2.5483100000
Cl42	0.3238090000	0.0080090000	-2.3154700000

TS0:

Fe1	-1.8959090000	0.0965180000	0.2630310000
N2	-1.7139240000	1.9122790000	-0.5852480000
N3	-0.7261620000	0.7316730000	1.7792580000
N4	-2.6660910000	-0.6140220000	-1.4579360000
N5	-1.6836560000	-1.7930660000	0.9131360000
C6	-2.2388120000	2.3098610000	-1.8085920000
C7	-0.3572220000	-0.0084920000	2.9008660000
C8	-1.1715500000	3.0600520000	-0.0185640000
C9	-0.3726600000	2.0505970000	2.0644940000
C10	-3.1130200000	0.1408560000	-2.5409580000
C11	-1.1192260000	-2.2007250000	2.1160200000
C12	-3.0820110000	-1.9184500000	-1.7104200000
C13	-2.1773710000	-2.9477210000	0.3179940000
C14	-2.0099660000	3.7209990000	-2.0105780000
C15	0.2476740000	0.8557200000	3.8831340000
C16	-1.3551910000	4.1845380000	-0.9054730000
C17	0.2387670000	2.1234730000	3.3682390000
C18	-3.8026770000	-0.7073630000	-3.4806150000
C19	-1.2593280000	-3.6300020000	2.2673840000
C20	-3.7854370000	-1.9748640000	-2.9691260000
C21	-1.9097680000	-4.0905470000	1.1591020000
H22	-2.3164430000	4.2700880000	-2.8886750000
H23	0.6217280000	0.5248120000	4.8409460000
H24	-1.0191500000	5.1898200000	-0.6970760000
H25	0.6014230000	3.0337840000	3.8233050000
H26	-4.2421360000	-0.3642090000	-4.4055780000
H27	-0.9003000000	-4.1922630000	3.1166270000
H28	-4.2045320000	-2.8744600000	-3.3950910000
H29	-2.1923670000	-5.1050030000	0.9195600000
C30	-2.9034480000	1.4968520000	-2.7098520000
C31	-0.5245430000	-1.3740680000	3.0517090000
C32	-2.8443610000	-3.0088220000	-0.8928050000
C33	-0.5619610000	3.1325920000	1.2218020000
H34	-3.2795250000	1.9563340000	-3.6168830000
H35	-0.1594440000	-1.8284760000	3.9658790000
H36	-3.2007360000	-3.9769950000	-1.2255250000
H37	-0.2157060000	4.1032750000	1.5592290000
O38	1.6950250000	-1.3701940000	-0.2945680000
C39	5.8164150000	-1.7641120000	-1.7541860000
C40	6.9130130000	-0.8948170000	-1.7048660000
C41	6.7994780000	0.3493400000	-1.0721590000
C42	5.5872930000	0.7335110000	-0.4801060000
C43	4.5193920000	-0.1561470000	-0.5515760000

C44	4.5962520000	-1.3961080000	-1.1712090000
H45	5.9039040000	-2.7273700000	-2.2457830000
H46	7.8548710000	-1.1852950000	-2.1581890000
H47	7.6473720000	1.0256100000	-1.0378690000
H48	5.4980340000	1.6996790000	0.0058620000
I49	2.5813500000	0.3064610000	0.3222530000
H50	3.7205540000	-2.0397690000	-1.1925020000
O51	0.3528850000	-0.3489300000	-2.4386180000
H52	-0.5700880000	-0.6608440000	-2.4376840000
H53	0.8415680000	-0.8079060000	-1.6991530000
Cl54	-3.9729300000	0.5167810000	1.3384370000

TS1:

Fe1	1.2214560000	0.1387390000	0.5435180000
N2	2.7959270000	0.2488390000	-0.6795270000
N3	1.3892590000	-1.8905280000	0.5988700000
N4	1.0356930000	2.1239970000	0.4886830000
N5	-0.3757440000	0.0088490000	1.7952660000
C6	3.3966580000	1.3974200000	-1.1702770000
C7	0.6535300000	-2.7692070000	1.3773580000
C8	3.5119340000	-0.8211550000	-1.2059450000
C9	2.3070660000	-2.6552030000	-0.0940260000
C10	1.8681450000	3.0253330000	-0.1612720000
C11	-0.8655290000	-1.1323770000	2.4099170000
C12	0.0399140000	2.8804670000	1.1018690000
C13	-1.1541680000	1.0580560000	2.2422120000
C14	4.5126580000	1.0409330000	-2.0184340000
C15	1.1200120000	-4.1210880000	1.1563010000
C16	4.5785040000	-0.3223010000	-2.0463340000
C17	2.1347530000	-4.0519810000	0.2430610000
C18	1.3789620000	4.3700180000	0.0407620000
C19	-1.9808960000	-0.7834660000	3.2636500000
C20	0.2511990000	4.2799080000	0.8105120000
C21	-2.1638700000	0.5661860000	3.1545280000
H22	5.1491480000	1.7535160000	-2.5221870000
H23	0.7171760000	-4.9961530000	1.6452770000
H24	5.2829330000	-0.9483190000	-2.5742840000
H25	2.7292600000	-4.8584210000	-0.1609230000
H26	1.8497800000	5.2579530000	-0.3552240000
H27	-2.5379880000	-1.4891610000	3.8626190000
H28	-0.3782830000	5.0807180000	1.1704170000
H29	-2.8996330000	1.1853750000	3.6464460000
C30	2.9796490000	2.6933870000	-0.9182190000
C31	-0.3858710000	-2.4203010000	2.2261180000
C32	-0.9778070000	2.3923650000	1.9018190000
C33	3.2817790000	-2.1610570000	-0.9511110000
H34	3.5439680000	3.5024080000	-1.3680230000
H35	-0.8676060000	-3.2177950000	2.7815440000
H36	-1.6710410000	3.1123490000	2.3227150000
H37	3.9376500000	-2.8797310000	-1.4303480000
O38	0.1054690000	0.0379920000	-0.9666690000
C39	-4.6415830000	1.7239800000	-0.8703700000
C40	-5.6272410000	0.9950730000	-0.1947190000
C41	-5.4418820000	-0.3691540000	0.0603560000
C42	-4.2715430000	-1.0115470000	-0.3627400000
C43	-3.3157140000	-0.2611590000	-1.0527040000
C44	-3.4635380000	1.1027540000	-1.3115040000
H45	-4.7811140000	2.7831420000	-1.0614040000
H46	-6.5357150000	1.4878580000	0.1362600000
H47	-6.1991820000	-0.9363030000	0.5917390000

H48	-4.1190370000	-2.0645330000	-0.1567150000
I49	-1.5339670000	-1.2566430000	-1.7480960000
H50	-2.6798300000	1.6698310000	-1.8165810000
O51	-0.7573020000	2.3149440000	-2.2736070000
H52	-0.4644490000	3.1288230000	-1.8248080000
H53	-0.3099390000	1.5372150000	-1.8457680000
Cl54	2.6308390000	0.2205430000	2.4818340000

Ethylbenzene:

C1	-0.1084190000	-0.0725050000	0.0584000000
C2	-0.0241480000	-0.2442470000	1.4510480000
C3	1.2079590000	-0.1781610000	2.1107630000
C4	2.3812580000	0.0613950000	1.3857520000
C5	2.3122480000	0.2325840000	-0.0018890000
C6	1.0778430000	0.1656230000	-0.6572410000
C7	-1.4504930000	-0.1043650000	-0.6493870000
C8	-2.1207740000	1.2855530000	-0.7284040000
H9	-0.9305980000	-0.4354500000	2.0198100000
H10	1.2524480000	-0.3172520000	3.1867960000
H11	3.3383880000	0.1099860000	1.8955370000
H12	3.2177540000	0.4137490000	-0.5732080000
H13	1.0323640000	0.2946530000	-1.7356570000
H14	-2.1236060000	-0.7982440000	-0.1289830000
H15	-1.3201490000	-0.4981840000	-1.6658940000
H16	-2.2933790000	1.6930130000	0.2743360000
H17	-3.0861990000	1.2264090000	-1.2445980000
H18	-1.4854390000	1.9947290000	-1.2712880000

PhIO:

C1	-0.1293880000	0.0000000000	0.1212180000
C2	-0.0546290000	0.0000000000	1.5105120000
C3	1.2210730000	0.0000000000	2.0940460000
C4	2.3667280000	0.0000000000	1.2876340000
C5	2.2495520000	0.0000000000	-0.1081550000
C6	0.9828450000	0.0000000000	-0.7086460000
I7	-2.0279000000	0.0000000000	-0.9618510000
O8	-1.2444730000	0.0000000000	-2.7978260000
H9	-0.9437430000	0.0000000000	2.1329190000
H10	1.3138510000	0.0000000000	3.1753790000
H11	3.3490410000	0.0000000000	1.7485950000
H12	3.1381970000	0.0000000000	-0.7310070000
H13	0.8376710000	0.0000000000	-1.7882340000

EB—PhIO:

C1	0.0501700000	0.0028060000	-0.1096320000
C2	0.0788390000	0.4053550000	1.2381390000
C3	1.2878960000	0.4436820000	1.9435790000
C4	2.4855700000	0.0790040000	1.3171010000
C5	2.4668740000	-0.3290770000	-0.0224660000
C6	1.2588520000	-0.3656190000	-0.7272380000
C7	-1.2553900000	0.0034820000	-0.8851810000
C8	-1.4186250000	1.2554330000	-1.7760350000
H9	-0.8591820000	0.6696770000	1.7225360000
H10	1.2945150000	0.7565240000	2.9842090000
H11	3.4222870000	0.1082360000	1.8659080000
H12	3.3901120000	-0.6200260000	-0.5154570000
H13	1.2510820000	-0.6855930000	-1.7666020000
H14	-2.0925550000	-0.0412970000	-0.1786820000
H15	-1.3095790000	-0.8932440000	-1.5189770000
H16	-1.4090970000	2.1658690000	-1.1663090000

H17	-2.3674140000	1.2230240000	-2.3249790000
H18	-0.6034170000	1.3311390000	-2.5057600000
O19	-3.1461530000	0.4574930000	2.1651970000
I20	-2.9761790000	-1.1442030000	3.3451720000
C21	-2.7604100000	-0.0319510000	5.2122700000
C22	-2.5694650000	-0.6639870000	6.4364330000
C23	-2.4430940000	0.1473190000	7.5742510000
C24	-2.5094110000	1.5415370000	7.4586110000
C25	-2.7024710000	2.1392130000	6.2066070000
C26	-2.8313840000	1.3452640000	5.0585230000
H27	-2.5168770000	-1.7441630000	6.5241340000
H28	-2.2925680000	-0.3148230000	8.5444900000
H29	-2.4102200000	2.1605710000	8.3440900000
H30	-2.7533840000	3.2195190000	6.1187340000
H31	-2.9830220000	1.7636020000	4.0653430000

PhI:

C1	0.3885990000	0.2552420000	-0.3524220000
C2	0.9920350000	1.4515220000	0.0447510000
C3	1.9246540000	2.0592780000	-0.8067280000
C4	2.2460760000	1.4752830000	-2.0369770000
C5	1.6326220000	0.2772360000	-2.4193830000
C6	0.6982360000	-0.3413070000	-1.5776660000
I7	-1.0472590000	-0.6878680000	0.9497640000
H8	0.7452730000	1.9061630000	0.9966720000
H9	2.3959730000	2.9884520000	-0.5026400000
H10	2.9688100000	1.9499930000	-2.6924280000
H11	1.8763730000	-0.1822620000	-3.3719710000
H12	0.2249620000	-1.2688870000	-1.8765830000

1-phenyl-ethanol:

C1	-0.0056540000	-0.0211680000	0.0313480000
C2	0.0286970000	-0.1630930000	1.4281790000
C3	1.2461520000	-0.1513660000	2.1158110000
C4	2.4470440000	-0.0025580000	1.4111640000
C5	2.4191290000	0.1310050000	0.0183300000
C6	1.2002510000	0.1225420000	-0.6699200000
C7	-1.3422950000	0.0119940000	-0.6858160000
C8	-2.0363860000	1.3783820000	-0.5605290000
H9	-0.8998530000	-0.2895400000	1.9799350000
H10	1.2578970000	-0.2643450000	3.1956030000
H11	3.3937930000	0.0030140000	1.9423810000
H12	3.3472740000	0.2384630000	-0.5349270000
H13	1.1694320000	0.2095570000	-1.7488010000
O14	-1.0995010000	-0.3017370000	-2.0922450000
H15	-1.9334700000	-0.2205590000	-2.5955150000
H16	-1.9951120000	-0.7615350000	-0.2507880000
H17	-2.2075650000	1.6367680000	0.4897630000
H18	-3.0097920000	1.3705420000	-1.0689490000
H19	-1.4100800000	2.1549560000	-1.0110030000

TS_{HA}:

C1	2.3109380000	0.3102160000	-2.6302140000
C2	3.6110760000	0.0793990000	-2.1380460000
C3	4.5322760000	-0.6668650000	-2.8760010000
C4	4.1717670000	-1.2033530000	-4.1199010000
C5	2.8790770000	-0.9957660000	-4.6132450000
C6	1.9561100000	-0.2507750000	-3.8708250000
C7	1.3258950000	1.1210690000	-1.8402410000
C8	1.7729820000	2.5276320000	-1.4440270000

H9	3.8800890000	0.4651040000	-1.1597940000
H10	5.5290900000	-0.8378280000	-2.4805450000
H11	4.8889790000	-1.7826470000	-4.6931400000
H12	2.5886250000	-1.4134640000	-5.5725700000
H13	0.9527820000	-0.0934650000	-4.2573370000
H14	1.1204920000	0.5017530000	-0.8442290000
H15	0.3433130000	1.1386780000	-2.3278370000
H16	2.7117490000	2.5006280000	-0.8837850000
H17	1.0217930000	3.0063650000	-0.8090620000
H18	1.9259830000	3.1509500000	-2.3356820000
O19	1.1220570000	0.3184150000	0.4453200000
I20	0.9267230000	-0.4505130000	2.4663500000
C21	-1.0925530000	0.2802100000	2.7456630000
C22	-1.8160530000	-0.0242740000	3.8971090000
C23	-3.1181240000	0.4838040000	4.0123320000
C24	-3.6617060000	1.2726510000	2.9911860000
C25	-2.9075580000	1.5585080000	1.8462300000
C26	-1.6053530000	1.0583010000	1.7138690000
H27	-1.3948690000	-0.6363480000	4.6872210000
H28	-3.7012190000	0.2590190000	4.8996760000
H29	-4.6699980000	1.6617670000	3.0878940000
H30	-3.3284820000	2.1690210000	1.0537350000
H31	-0.9862290000	1.2489280000	0.8418090000