Supporting Information

Origin of the Catalytic Effects of Molecular Iodine: A Computational Analysis

Martin Breugst,[‡*] Eric Detmar,[‡] and Daniel von der Heiden[‡]

[‡] Universität zu Köln, Department für Chemie, Greinstraße 4, 50939 Köln, Germany.

mbreugst@uni-koeln.de

Table of Contents

1 Experimental Details S2

2 Computational Details S8

3 Variation of the Computational Method S10

4 Noncovalent Interaction Analysis S11

5 Complexation Reactions between Carbonyls and Iodine in CCl_4 ..... S12

6 Complexation Reactions between Carbonyls and Iodine in CH_2Cl_2 ..... S18

7 Intramolecular Aza-Michael Reaction S24

8 Intermolecular Aza-Michael Reaction S31

9 Friedel-Crafts Reaction S40

10 Michael Addition to Nitrostyrene S50

11 Decomposition of Iodine S56

12 HI-Catalyzed Friedel-Crafts Reaction S58

13 References S61

1 Experimental Details

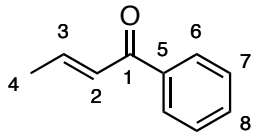
1.1 General

Commercially available indole, iodine, and aqueous HI (57 wt-% in water) were used without further purification. HPLC-grade acetonitrile (water content < 20 ppm) was freshly distilled over CaH_2. All experiments were conducted in the dark under argon atmosphere.

Chemical shifts in the ^1H and ^{13}C NMR spectra are given in ppm and refer either to CD_2Cl_2 (δ_H = 5.32, δ_C = 53.8) or CD_3CN (δ_H = 1.94, δ_C = 118.3).[1] Coupling constants are given in Hz. Signal assignments are based on additional COSY, gHSQC, or gHMBC experiments.

1.2 Synthesis of 1-Phenylbut-2-en-1-one (16)

1-Phenylbut-2-en-1-one (**16**) was prepared following a modified procedure of Moody and coworkers:[2] Aluminium chloride (13.6 g, 102 mmol) was added to cooled solution of *trans*-crotonyl chloride (6.50 g, 62.2 mmol) in benzene (18 mL) and stirred overnight. The reaction was deactivated by addition of 1 M aqueous HCl (300 mL) and ice (200 mL). The resulting mixture was extracted with dichloromethane (3 × 50 mL), washed with 1 M aqueous NaOH (20 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on SiO_2 (ethyl acetate/cyclohexane 1:13 (v/v); R_f = 0.44) to give 1-phenylbut-2-en-1-one (**16**) as a colorless oil (5.72 g, 39.1 mmol, 63 %).

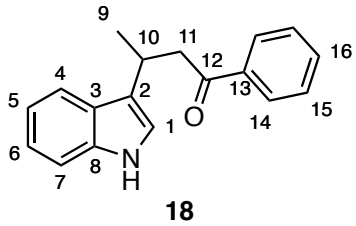


16

^1H NMR (CD_2Cl_2, 300 MHz) δ = 1.99 (dd, ^3J = 6.6 Hz and ^4J = 1.2 Hz, 3 H, 4–H), 6.91–6.97 (m, 1 H, 2–H), 7.01–7.13 (m, 1 H, 3–H), 7.45–7.51 (m, 2 H, 7–H), 7.54–7.59 (m, 1 H, 8–H), 7.93–7.96 (m, 2 H. 6–H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz) δ = 18.7 (C–4), 127.7 (C–2), 128.7, 128.9 (C–6 and C–7), 132.9 (C–8), 138.4 (C–5), 145.2 (C–3), 190.5 (C–1). IR (neat, ATR) $\tilde{\nu}$ [cm^{-1}] = 3057 (w), 2970 (w), 2913 (w), 2361 (w), 1668 (m), 1651 (m), 1622 (s), 1447 (m), 1331 (w), 1294 (s), 1217 (s), 962 (m), 916 (m), 813 (w), 756 (m), 691 (s), 662 (m). HR-MS (ESI) $[M+H]^+$: *m*/*z* calcd for $C_{10}H_{11}O^+$: 147.08044 found 147.08049.

1.3 Solvent-Free Reaction between Indole (17) and 1-Phenylbut-2-en-1-one (16)

To obtain reference material, we followed the published protocol of Banik and coworkers[3] to synthesize adduct **18**: Indol (**17**, 121 mg, 1.03 mmol) and *trans*-1-phenylbut-2-en-1-one (**16**, 150 mg, 1.03 mmol) were mixed without any solvent and iodine (14 mg, 55 µmol) was added. After the addition, the mixture is getting warm and solidifies. After 30 min, the reaction was dilluted with dichloromethane (25 mL), washed with saturated, aqueous $Na_2S_2O_3$ solution (10 mL), and water (20 mL). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on SiO_2 (ethyl acetate/cyclohexane 1:4 (v/v); $R_f = 0.32$) to give the desired product **18** (180 mg, 0.684 mmol, 66 %) as a yellow solid.



18

Melting point: 105.5 °C (Lit:[4] 103–105 °C). ^{1}H NMR (CD_2Cl_2, 300 MHz) $\delta = 1.48$ (d, $^3J = 6.4$ Hz, 3 H, 9–H), 3.29 (dd, $^2J = 16.4$ Hz and $^3J = 8.5$ Hz, 1 H, 11–H), 3.51 (dd, $^2J = 16.4$ Hz and $^3J = 5.4$ Hz, 1 H, 11–H'), 3.79–3.91 (m, 1 H, 10–H), 7.03 (d, $^3J = 2.2$ Hz, 1 H, 1–H), 7.10–7.15 (m, 1 H, 5–H), 7.18–7.25 (m, 1 H, 6–H), 7.38(d, $^3J = 8.0$ Hz, 1 H, 7–H), 7.45–7.50 (m, 2 H, 15–H), 7.56–7.61 (m, 1 H, 16–H), 7.70 (d, $^3J = 7.8$ Hz, 1 H, 4–H), 7.97–8.00 (m, 2 H, 14–H), 8.00 (br s, 1 H, NH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz) $\delta = 21.4$ (C–9), 27.5 (C–10), 46.8 (C–11), 111.7 (C7), 119.5 (C–4/C–5 superimposed), 120.7 (C–1), 121.7 (C–2), 122.2 (C–6), 126.8 (C–3), 128.4 (C–14), 128.9 (C–15), 133.3 (C–16), 137.0 (C–8), 137.8 (C–13), 200.0 (C–12). IR (neat, ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3354 (m), 3055 (w), 2984 (w), 2961 (w), 2872 (w), 1667 (s), 1618 (w), 1593 (w), 1574(w), 1445 (m), 1339 (m), 1215 (s), 997 (m), 746 (s), 696 (m). HR-MS (ESI) $[M+H]^+$: *m*/*z* calcd for $C_{18}H_{18}NO^+$: 264.13829 found 264.13854.

1.4 Comparison between Iodine Catalysis and HI Catalysis

General Procedure:

Fresh solutions were employed for each experiment and HI stock solutions were titrated with 0.1 M aqueous NaOH against methyl red prior to each experiment. A solution of equimolar amounts of *trans*-1-phenylbut-2-en-1-one (**16**) and indole (**17**) in dry acetonitrile was mixed with the same volume of a solution of the catalyst (either I_2 or aqueous HI) in dry acetonitrile. After mixing, the effective concentrations of the reactants **16** and **17** are approx. 0.5 M each, and the catalyst concentration is ca 25 mM (5 mol-%). After 3 minutes, 1 mL of a deactivating solution (1:1 (v/v) mixture of a saturated, aqueous $Na_2S_2O_3$ solution and 0.2 M aqueous NaOH) was added. The mixture was subsequently diluted

with ethylacetate (80 mL) and deactivating solution (9 mL). The organic layer was washed with water (2 × 10 mL) and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on SiO_2 to give the desired product **18**.

Iodine Catalysis:

The iodine-catalyzed reaction was carried out four times with freshly prepared stock solutions. The results are summarized in Table S1.

Table S1: Detailed Parameters for the Iodine-Catalyzed Reaction between **16** and **17** (CH_3CN, 23 °C).

Run	**16**	**17**	Iodine	**18**
1	58.4 mg (0.399 mmol)	46.9 mg (0.400 mmol)	5.0 mg (20 µmol)	77 mg (0.29 mmol, 73 %)
2	59.7 mg (0.408 mmol)	46.9 mg (0.400 mmol)	5.1 mg (20 µmol)	77 mg (0.29 mmol, 73%)
3	74.6 mg (0.510 mmol)	58.6 mg (0.500 mmol)	6.4 mg (25 µmol)	101 mg (0.384 mmol, 77 %)
4	58.4 mg (0.399 mmol)	47.0 mg (0.401 mmol)	5.1 mg (20 µmol)	74 mg (0.28 mmol, 70%)
Average Yield: 73 ± 3 %				

HI Catalysis:

The HI-catalyzed reaction was carried out four times with freshly prepared stock solutions. HI stock solutions were titrated prior to use. The results are summarized in Table S2.

Table S2: Detailed Parameters for the HI-Catalyzed Reaction between **16** and **17** (CH_3CN, 23 °C).

Run	**16**	**17**	HI	**18**
1	58.4 mg (0.399 mmol)	47.0 mg (0.401 mmol)	2.6 mg (20 µmol)	39 mg (0.15 mmol, 37 %)
2	74.6 mg (0.510 mmol)	58.6 mg (0.500 mmol)	3.2 mg (25 µmol)	57 mg (0.22 mmol, 43 %)
3	58.4 mg (0.399 mmol)	46.9 mg (0.400 mmol)	2.6 mg (20 µmol)	45 mg (0.17 mmol, 43 %)
4	59.7 mg (0.408 mmol)	46.9 mg (0.400 mmol)	2.6 mg (20 µmol)	41 mg (0.16 mmol, 39 %)
Average Yield: 40 ± 3 %				

NMR Comparison:

Stock solutions of *trans*-1-phenylbut-2-en-1-one (**16**) and indole (**17**) in CD_3CN were mixed with fresh solutions of either iodine or HI in CD_3CN. The reaction was started by injection of the catalyst solution to the substrate solution under argon atmosphere. Complete mixing was achieved by vortex mixing. NMR spectra were recorded immediately after mixing on a 600 MHz instrument at 23 °C. ^{1}H NMR

spectra were recorded every 20–30 s. Product formation was detected from the integrals of characteristic signals for reactants and products (usually the terminal methyl group of **16** and **18** as these signals did not overlap with any other) using the following equation:

$$\text{yield} = \frac{\text{int}(\mathbf{18})}{\text{int}(\mathbf{18}) + \text{int}(\mathbf{16})}$$

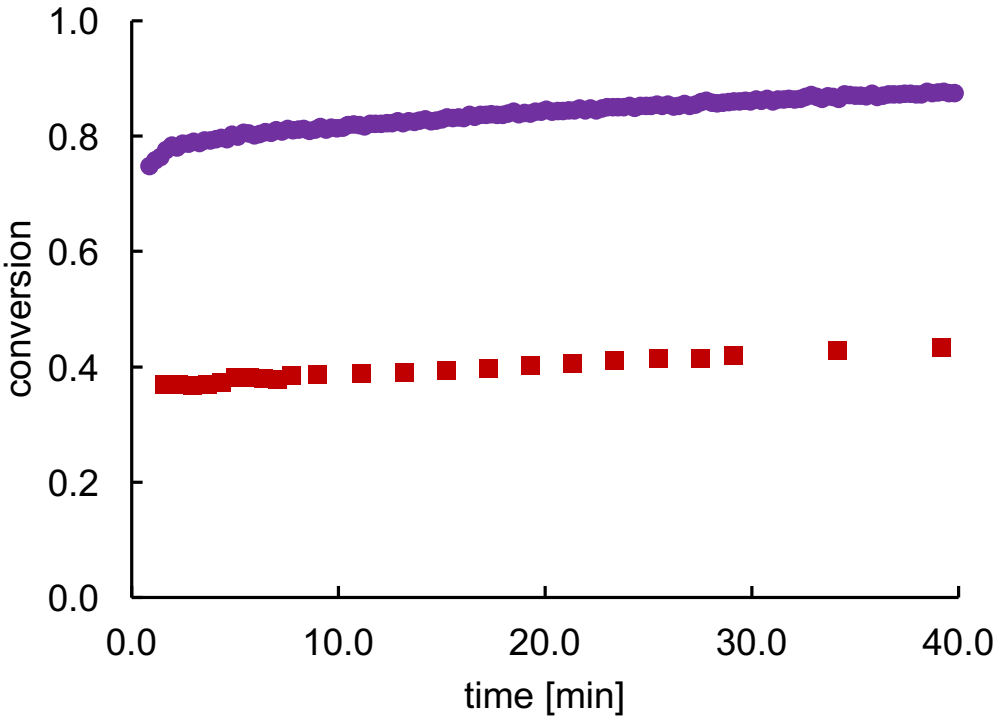
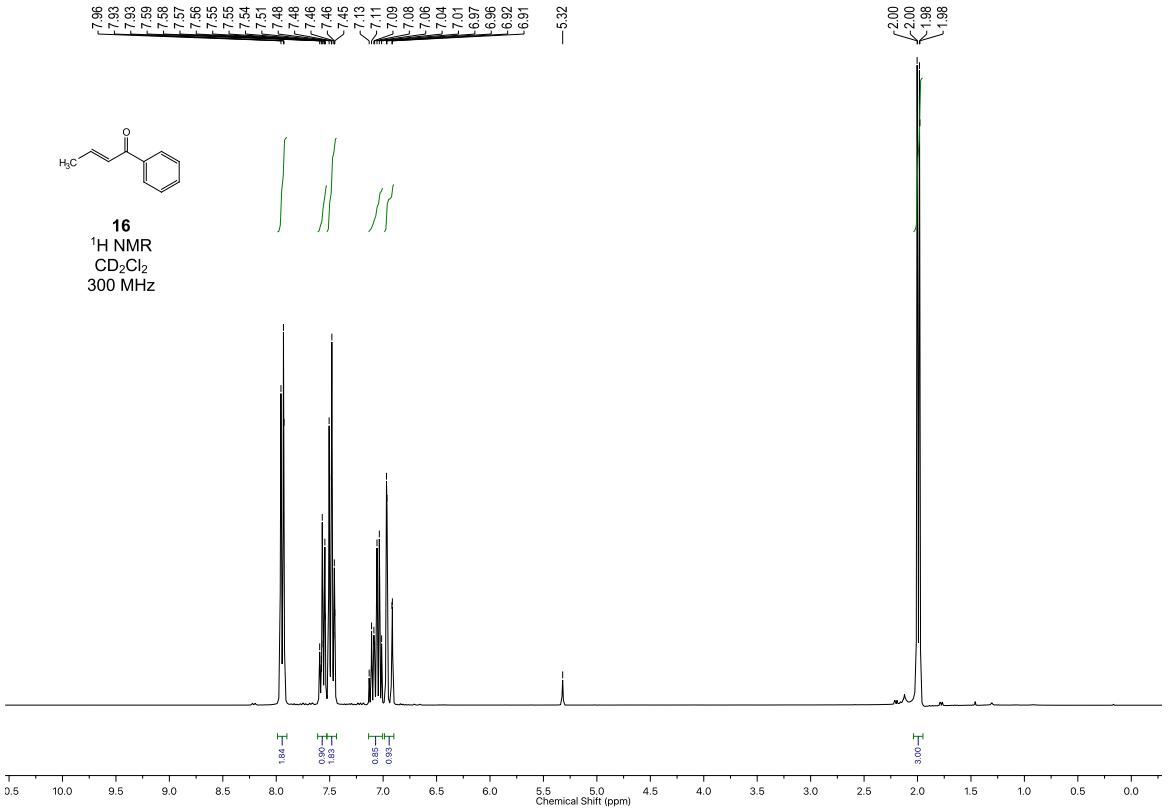
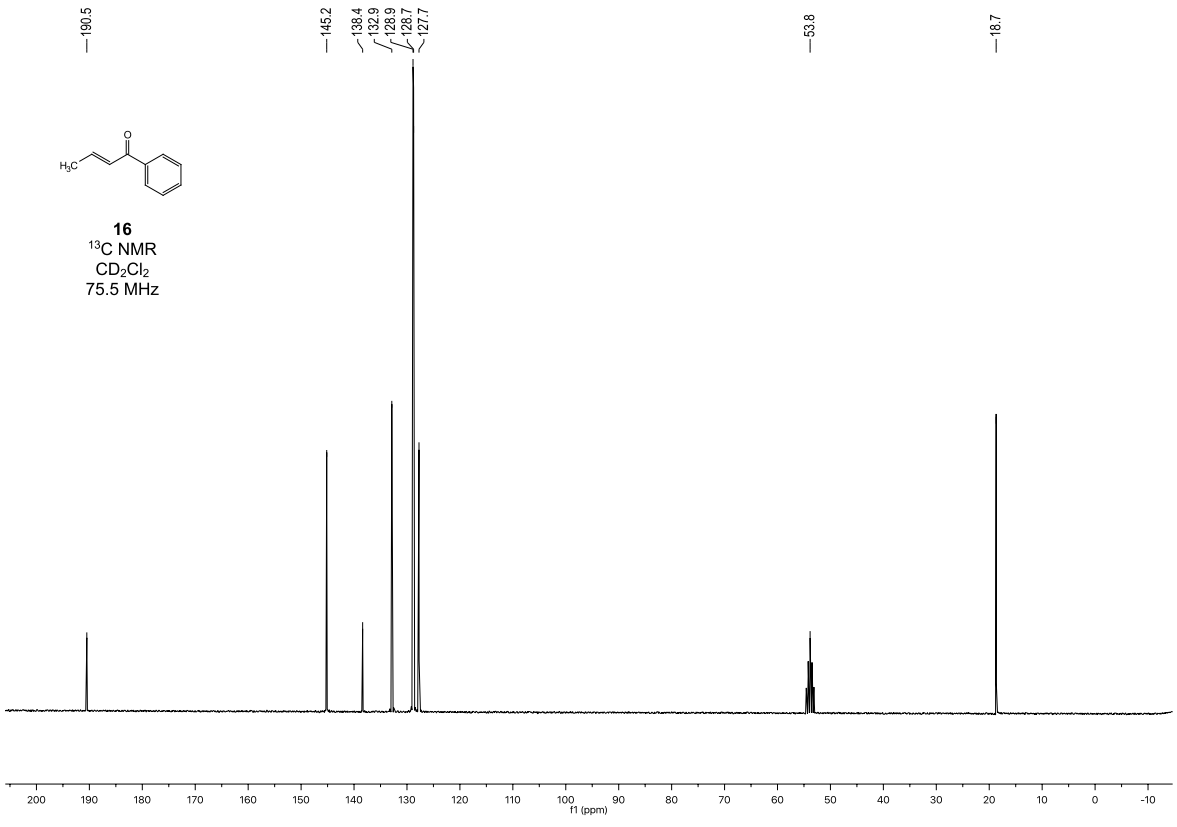
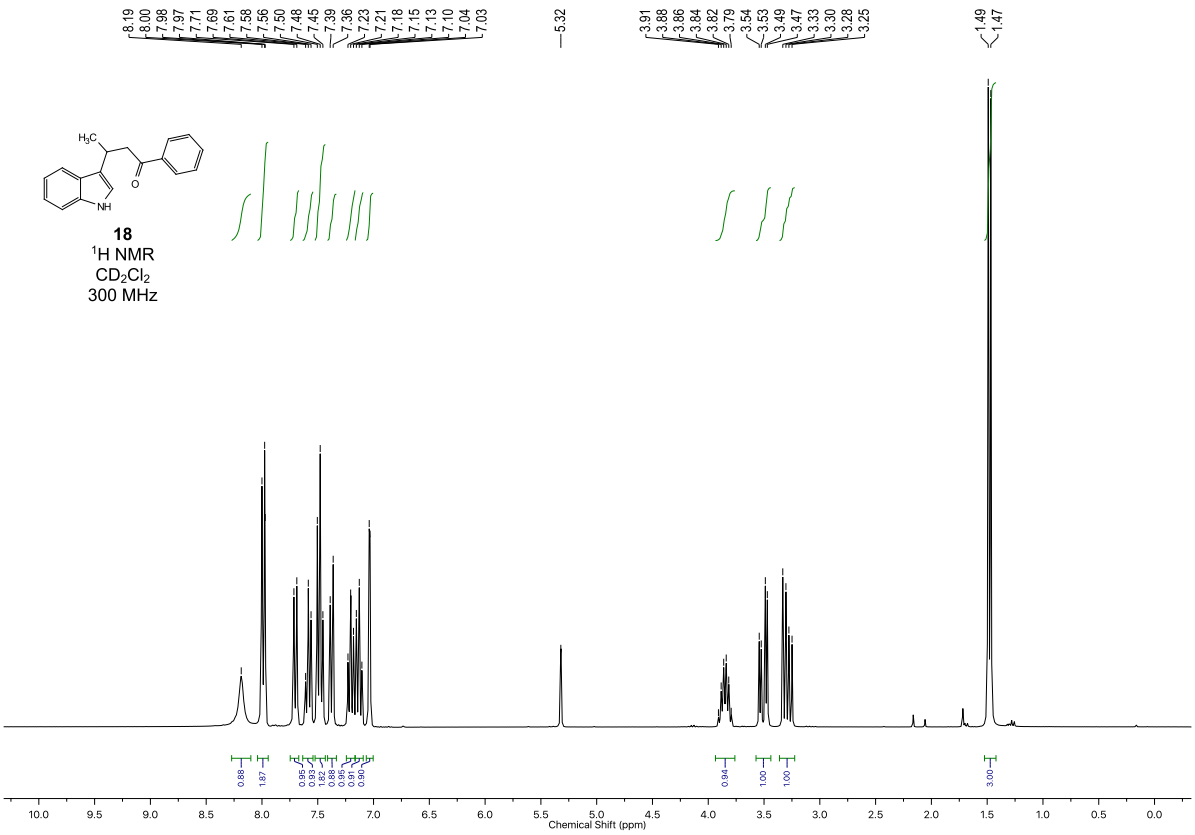


Figure S1: NMR kinetics for the iodine-catalyzed (purple) and HI-catalyzed (red) reaction between *trans*-1-phenylbut-2-en-1-one (**16**) and indole (**17**) in CD_3CN at 23 °C (concentrations: [**16**] = [**17**] = 0.50 mol L^{-1}, $[I_2]$ = 1.5 mmol L^{-1} (3 mol-%), [HI] = 1.5 mmol L^{-1} (3 mol-%)).

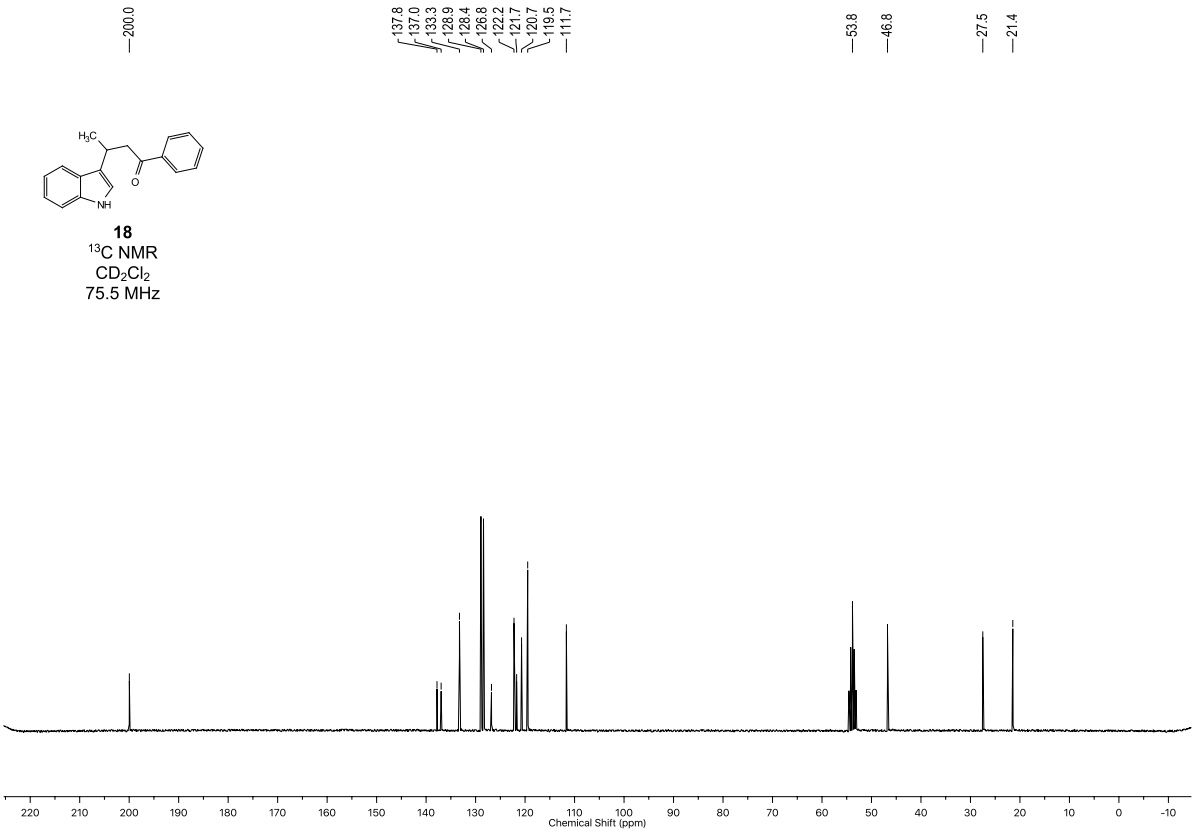
Copies of NMR Spectra:







18
^{1}H NMR
CD_2Cl_2
300 MHz



18
^{13}C NMR
CD_2Cl_2
75.5 MHz

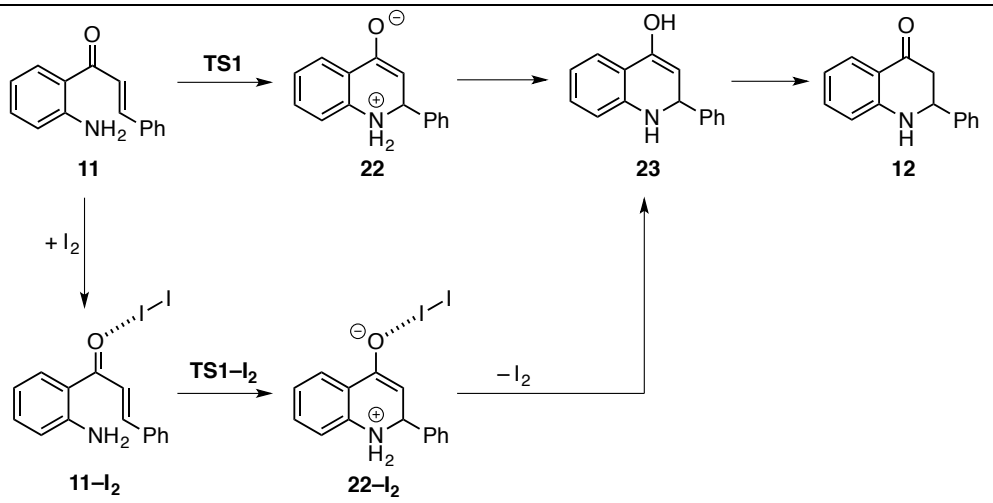
2 Computational Details

The conformational space for all intermediates of the iodine-catalyzed reactions was explored using the OPLS-2005 force field[5] and a modified Monte-Carlo search routine implemented in MacroModel version 10.6.[6] An energy cut-off of 20 kcal mol^{-1} was chosen for the conformational analysis and structures with heavy-atom root-mean-square deviations (RMSD) less than 1 Å after the initial force field optimizations were considered to be the same conformer. The remaining structures were subsequently optimized with meta-hybrid M06-2X functional,[7] Grimme's D3 correction (zero-damping),[8] the triple-ζ basis set 6-311+G(d,p) for all atoms except Br and I, and the aug-cc-pVTZ basis set with the corresponding pseudopotential (commonly called aug-cc-pVTZ-PP) for Br and I.[9] Solvation by dichloromethane was accounted for by using the integral equation formalism polarizable continuum model (IEFPCM)[10] as indicated. Selected optimizations have also been performed with the dispersion-corrected functionals M06-L[11] or ωB97X-D[12] under otherwise identical conditions. Vibrational analysis verified that each structure was a minimum or transition state. Following intrinsic reaction coordinates (IRC) confirmed that all transition states connected the corresponding minima on the potential energy surface. Thermal corrections were calculated form unscaled harmonic vibrational frequencies at the same level of theory and refer to a standard state of 298.15 K and 1 mol L^{-1}. Entropic contributions to the reported free energies were obtained from partition functions evaluated with Truhlar's quasi-harmonic approximation.[13] This method uses the same approximations as the usual harmonic oscillator approximation except that all vibrational frequencies lower than 100 cm^{-1} are set equal to 100 cm^{-1}. Energies were subsequently calculated with single-point calculations employing the double-hybrid B2PLYP functional,[14] Grimme's D3 correction (zero-damping),[8] the large triple-ζ basis set aug-cc-pVTZ for all atoms, the aug-cc-pVTZ-PP pseudopotential for Br and I and, if indicated, IEFPCM for dichloromethane.[10] An ultrafine grid corresponding to 99 radial shells and 590 angular points was used throughout this investigation for the numerical integration of the density. All DFT

calculations were performed with Gaussian 09,[15] natural population analysis used the NBO 6.0 program[16] in combination with Gaussian 09. The NCIPLOT code was employed for the visualization non-covalent interactions.[17]

3 Variation of the Computational Method

Table S3: Variation of the Computational Method for the Intramolecular Aza-Michael-Reaction of **11** (The aug-cc-pVTZ-PP Pseudopotential Was Used for Iodine in all Cases).



Method	**11**	**11–I_2**	**TS1**	**TS1–I_2**	**22**	**22–I_2**	**23**	**12**
B2PLYP-D3/aug-cc-pVTZ/IEFPCM// M06-2X-D3/6-311+G(d,p)/IEFPCM	0.0	+1.3	+32.3	+26.6	+29.2	+18.3	+5.8	–8.3
B2PLYP-D3/aug-cc-pVTZ/IEFPCM// M06-2X-D3/6-311+G(d,p)	0.0	+1.4	+32.5	+28.1	+29.6	+20.2	+5.7	–8.3
B2PLYP-D3/aug-cc-pVTZ/IEFPCM// M06-L-D3/6-311+G(d,p)	0.0	+1.3	+30.9	+26.1	+29.4	+20.3	+6.0	–7.9
B2PLYP-D3/aug-cc-pVTZ/IEFPCM// ωB97XD3/6-311+G(d,p)	0.0	+3.5	+34.3	+30.0	+31.5	+22.6	+7.8	–6.2
B2PLYP-D3/aug-cc-pVTZ// M06-2X-D3/6-311+G(d,p)	0.0	+0.5	+41.0	+34.8	+41.0	+32.2	+5.7	–7.5
B2PLYP-D3/aug-cc-pVTZ// M06-L-D3/6-311+G(d,p)	0.0	+0.5	+41.1	+34.7	+40.6	+32.1	+5.9	–7.2
B2PLYP-D3/aug-cc-pVTZ// ωB97XD3/6-311+G(d,p)	0.0	+2.5	+43.0	+36.8	+43.0	+34.4	+7.7	–5.6

4 Noncovalent Interaction Analysis

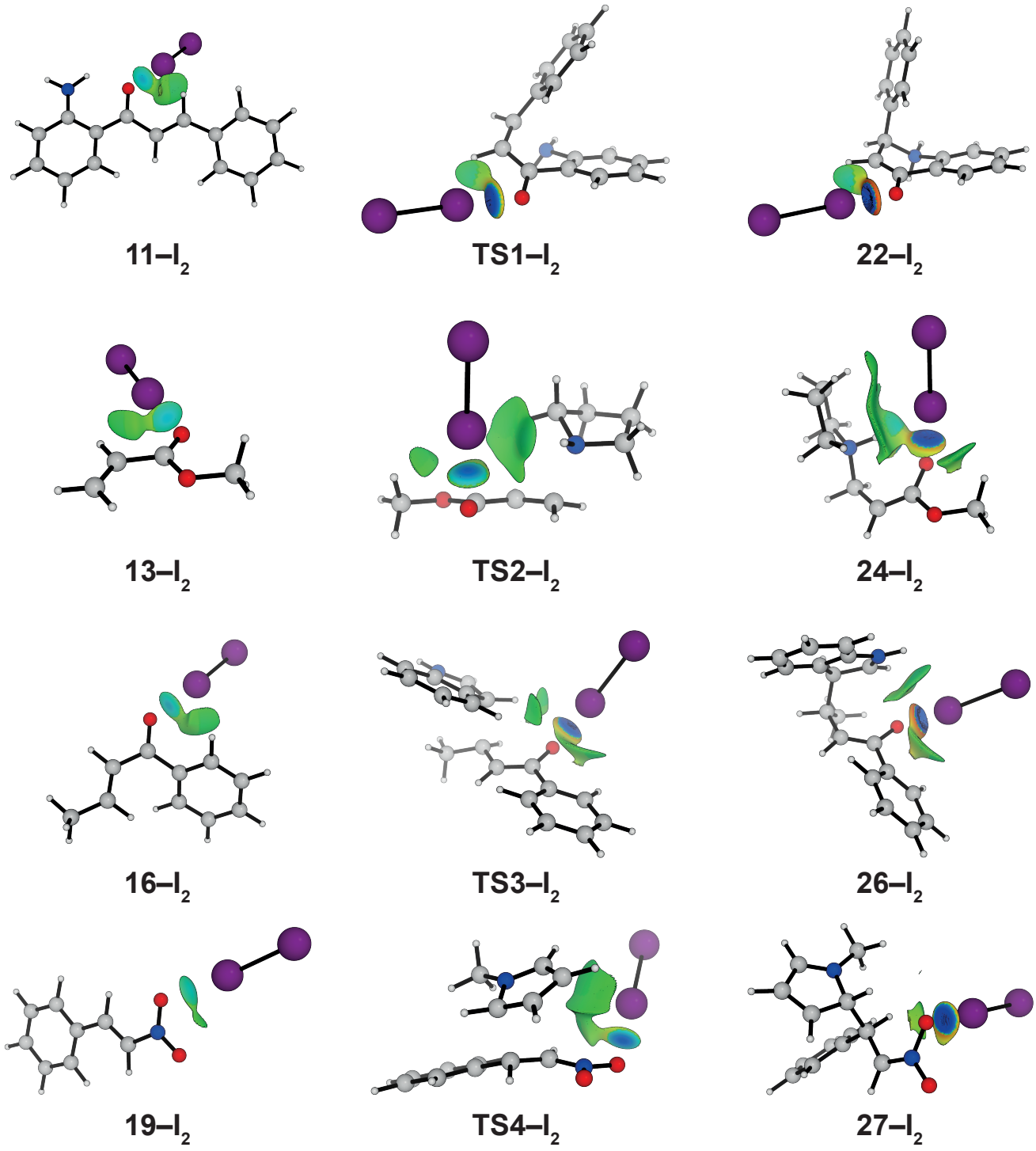


Figure S2: Noncovalent interaction (NCI) analysis for selected intermediates and transition states for the four model reactions. The gradient isosurfaces (s = 0.5 a.u.) are colored according to the sign $(\lambda_2)\rho$ over the range of –0.05 (blue) to +0.05 (red).

5 Complexation Reactions between Carbonyls and Iodine in CCl_4

5.1 Acetone

SCF energy:	–193.099919 hartree
Zero-point correction:	+0.084191 hartree
Enthalpy correction:	+0.090453 hartree
Free energy correction:	+0.056262 hartree
Quasiharmonic free energy correction:	+0.056417 hartree

Cartesian Coordinates

C	-0.00001	0.18495	0.00000
C	1.28378	-0.61156	-0.00233
C	-1.28377	-0.61156	0.00233
O	0.00000	1.39326	0.00000
H	2.13685	0.04987	-0.13831
H	1.26056	-1.36785	-0.79020
H	1.37842	-1.14051	0.95008
H	-2.13687	0.04984	0.13831
H	-1.26054	-1.36786	0.79019
H	-1.37840	-1.14051	-0.95008

5.2 Iodine

SCF energy:	–590.956253 hartree
Zero-point correction:	+0.000531 hartree
Enthalpy correction:	+0.004346 hartree
Free energy correction:	–0.025152 hartree
Quasiharmonic free energy correction:	–0.025152 hartree

Cartesian Coordinates

I	0.00000	0.00000	1.33069
I	0.00000	0.00000	-1.33069

5.3 Acetone-Iodine Complex

SCF energy:	–784.068226 hartree
Zero-point correction:	+0.085607 hartree
Enthalpy correction:	+0.096355 hartree
Free energy correction:	+0.045084 hartree
Quasiharmonic free energy correction:	+0.047973 hartree

Cartesian Coordinates

C	3.81004	0.08444	-0.00144
C	3.57984	1.57274	-0.02635
C	5.23903	-0.38315	0.08112
O	2.89257	-0.70957	-0.03769
I	0.13526	-0.25888	-0.02136
I	-2.51829	0.13918	0.01670
H	2.56986	1.80225	-0.36125
H	4.31671	2.06713	-0.66153
H	3.71525	1.95671	0.98946

H	5.27747	-1.45111	0.28342
H	5.77621	0.17448	0.85133
H	5.73128	-0.17272	-0.87272

5.4 Acetophenone

SCF energy:	–384.779482 hartree
Zero-point correction:	+0.138723 hartree
Enthalpy correction:	+0.147473 hartree
Free energy correction:	+0.105858 hartree
Quasiharmonic free energy correction:	+0.106527 hartree

Cartesian Coordinates

C	1.69664	-0.20545	-0.00008
C	2.54085	1.04716	0.00024
C	0.20236	-0.06186	-0.00003
O	2.20856	-1.30301	-0.00026
C	-0.42197	1.18702	-0.00014
C	-1.81033	1.27562	-0.00012
C	-2.58033	0.11727	0.00002
C	-1.96262	-1.13234	0.00014
C	-0.57807	-1.22093	0.00011
H	-0.07817	-2.18188	0.00018
H	-3.66178	0.18682	0.00004
H	-2.56315	-2.03403	0.00027
H	0.16749	2.09600	-0.00021
H	-2.28933	2.24720	-0.00022
H	3.59062	0.76363	-0.00004
H	2.32346	1.65326	0.88275
H	2.32319	1.65418	-0.88155

5.5 Acetophenone-Iodine Complex

SCF energy:	–975.748326 hartree
Zero-point correction:	+0.139939 hartree
Enthalpy correction:	+0.153367 hartree
Free energy correction:	+0.094237 hartree
Quasiharmonic free energy correction:	+0.099610 hartree

Cartesian Coordinates

C	-2.49724	0.55712	0.00134
C	-2.15378	2.02432	0.00128
C	-3.93627	0.15109	0.00024
O	-1.62746	-0.29417	0.00230
C	-4.96653	1.09417	-0.00116
C	-6.29331	0.67830	-0.00216
C	-6.59541	-0.67965	-0.00175
C	-5.57114	-1.62507	-0.00035
C	-4.24712	-1.21191	0.00063
H	-3.43697	-1.93078	0.00172
H	-7.62967	-1.00292	-0.00252
H	-5.80835	-2.68197	-0.00004
H	-4.74267	2.15401	-0.00151
H	-7.08936	1.41272	-0.00326
I	1.16484	-0.13650	0.00089

I	3.84493	-0.02751	-0.00098
H	-1.07255	2.14435	0.00213
H	-2.57746	2.51044	0.88295
H	-2.57604	2.51007	-0.88128

5.6 Benzophenone

SCF energy: –576.457335 hartree
Zero-point correction: +0.192673 hartree
Enthalpy correction: +0.204311 hartree
Free energy correction: +0.155187 hartree
Quasiharmonic free energy correction: +0.156333 hartree

Cartesian Coordinates

C	-0.00003	1.11391	0.00017
C	1.29349	0.35844	0.03095
C	-1.29350	0.35840	-0.03087
O	-0.00008	2.32721	0.00040
C	1.41495	-0.87730	0.67000
C	2.65197	-1.51044	0.73074
C	3.76491	-0.92264	0.13753
C	3.64747	0.31021	-0.50139
C	2.41879	0.95460	-0.54302
C	-1.41471	-0.87754	-0.66952
C	-2.65168	-1.51083	-0.73036
C	-3.76483	-0.92286	-0.13779
C	-3.64767	0.31029	0.50068
C	-2.41908	0.95475	0.54247
H	-2.31206	1.92244	1.01790
H	-4.72557	-1.42257	-0.17742
H	-4.51547	0.76888	0.95918
H	-0.55020	-1.33306	-1.13817
H	-2.74584	-2.46190	-1.24035
H	0.55059	-1.33265	1.13909
H	2.74640	-2.46131	1.24105
H	2.31162	1.92210	-1.01883
H	4.72569	-1.42228	0.17709
H	4.51509	0.76870	-0.96031

5.7 Benzophenone-Iodine Complex

SCF energy: –1167.427584 hartree
Zero-point correction: +0.193753 hartree
Enthalpy correction: +0.210113 hartree
Free energy correction: +0.143971 hartree
Quasiharmonic free energy correction: +0.150094 hartree

Cartesian Coordinates

C	2.21372	-0.15946	-0.39736
C	2.02181	1.30421	-0.17631
C	3.53409	-0.78844	-0.10200
O	1.29437	-0.84259	-0.81775
C	2.60392	1.96288	0.90924
C	2.33858	3.31030	1.12543
C	1.51388	4.00704	0.24713

C	0.93783	3.35475	-0.84072
C	1.17997	2.00330	-1.04483
C	4.72928	-0.06963	-0.18527
C	5.94158	-0.71025	0.04552
C	5.96255	-2.06179	0.37577
C	4.77219	-2.78210	0.45914
C	3.56237	-2.15086	0.20924
H	2.62755	-2.69651	0.25464
H	6.90786	-2.55684	0.56437
H	4.79116	-3.83463	0.71425
H	4.71392	0.98039	-0.45212
H	6.86834	-0.15526	-0.03360
H	3.24097	1.41736	1.59577
H	2.77463	3.81545	1.97857
H	0.72816	1.47895	-1.87894
H	1.31623	5.05956	0.41228
H	0.29599	3.89817	-1.52327
I	-1.45695	-0.51650	-0.28825
I	-4.06174	-0.31341	0.31015

5.8 Benzaldehyde

SCF energy:	–345.473268 hartree
Zero-point correction:	+0.110584 hartree
Enthalpy correction:	+0.117852 hartree
Free energy correction:	+0.079979 hartree
Quasiharmonic free energy correction:	+0.079979 hartree

Cartesian Coordinates

C	-1.98843	0.46613	0.00020
C	-0.52953	0.20715	0.00014
O	-2.83325	-0.39416	-0.00037
C	0.35297	1.28622	0.00002
C	1.72545	1.06151	-0.00013
C	2.20873	-0.24326	-0.00011
C	1.32636	-1.32489	0.00006
C	-0.04219	-1.10216	0.00017
H	-0.03769	2.29900	0.00007
H	2.41449	1.89713	-0.00027
H	-0.74812	-1.92458	0.00026
H	3.27773	-0.42128	-0.00022
H	1.71223	-2.33709	0.00011
H	-2.27284	1.53597	0.00081

5.9 Benzaldehyde-Iodine Complex

SCF energy:	–936.441264 hartree
Zero-point correction:	+0.111882 hartree
Enthalpy correction:	+0.123777 hartree
Free energy correction:	+0.068633 hartree
Quasiharmonic free energy correction:	+0.072898 hartree

Cartesian Coordinates

C	2.42684	-0.22472	-0.00026
C	3.90003	-0.18608	-0.00006

O	1.72103	0.76048	-0.00023
C	4.60865	-1.38749	-0.00012
C	5.99869	-1.37140	0.00003
C	6.67199	-0.15366	0.00026
C	5.96382	1.04947	0.00035
C	4.57799	1.03637	0.00019
H	4.00457	1.95586	0.00024
H	7.75556	-0.13876	0.00037
H	6.49819	1.99152	0.00055
H	4.06977	-2.32943	-0.00025
H	6.55424	-2.30088	-0.00004
I	-1.04511	0.32258	-0.00019
I	-3.66268	-0.25849	0.00017
H	1.97396	-1.23348	-0.00042

5.10 Methyl Acetate

SCF energy:	–268.326820 hartree
Zero-point correction:	+0.090553 hartree
Enthalpy correction:	+0.097602 hartree
Free energy correction:	+0.060716 hartree
Quasiharmonic free energy correction:	+0.061457 hartree

Cartesian Coordinates

C	-1.79582	-0.51234	0.00011
C	-0.45987	0.17385	-0.00034
O	0.54515	-0.71546	-0.00009
C	1.86420	-0.16244	0.00010
H	2.54075	-1.01244	0.00026
H	2.01781	0.44974	-0.88849
H	2.01752	0.44985	0.88866
O	-0.28071	1.36354	0.00005
H	-2.58616	0.23333	0.00028
H	-1.87802	-1.14973	0.88128
H	-1.87849	-1.14986	-0.88091

5.11 Methyl-Acetate-Iodine Complex

SCF energy:	–859.294344 hartree
Zero-point correction:	+0.091825 hartree
Enthalpy correction:	+0.103467 hartree
Free energy correction:	+0.048948 hartree
Quasiharmonic free energy correction:	+0.053281 hartree

Cartesian Coordinates

C	3.25597	1.92856	0.00041
C	3.50819	0.45071	-0.00224
O	4.80862	0.16604	0.01673
C	5.14907	-1.22669	0.01587
H	6.23430	-1.26203	0.03268
H	4.73302	-1.71456	0.89666
H	4.76089	-1.70667	-0.88182
O	2.65774	-0.41070	-0.01952
I	-0.14155	-0.17803	-0.00890
I	-2.81248	0.04323	0.00677

H	2.18627	2.12150	-0.01548
H	3.73305	2.37766	-0.87151
H	3.70553	2.37008	0.89063

6 Complexation Reactions between Carbonyls and Iodine in CH_2Cl_2

6.1 Acetone

SCF energy:	–193.102782 hartree
Zero-point correction:	+0.084140 hartree
Enthalpy correction:	+0.090382 hartree
Free energy correction:	+0.056279 hartree
Quasiharmonic free energy correction:	+0.056357 hartree

Cartesian Coordinates

C	-0.00001	0.18306	0.00002
C	1.28227	-0.61121	-0.00243
C	-1.28231	-0.61115	0.00243
O	0.00006	1.39460	-0.00000
H	2.13706	0.04694	-0.14394
H	1.25445	-1.37214	-0.78536
H	1.37671	-1.13543	0.95258
H	-2.13708	0.04696	0.14429
H	-1.25437	-1.37237	0.78507
H	-1.37688	-1.13499	-0.95277

6.2 Iodine

SCF energy:	–590.956970 hartree
Zero-point correction:	+0.000530 hartree
Enthalpy correction:	+0.004346 hartree
Free energy correction:	–0.025153 hartree
Quasiharmonic free energy correction:	–0.025153 hartree

Cartesian Coordinates

I	0.00000	0.00000	1.33114
I	0.00000	0.00000	-1.33114

6.3 Acetone-Iodine Complex

SCF energy:	–784.071245 hartree
Zero-point correction:	+0.085583 hartree
Enthalpy correction:	+0.096295 hartree
Free energy correction:	+0.045359 hartree
Quasiharmonic free energy correction:	+0.047973 hartree

Cartesian Coordinates

C	3.79991	0.07539	-0.00124
C	3.58525	1.56381	-0.02403
C	5.22152	-0.40774	0.07991
O	2.87171	-0.71057	-0.03837
I	0.14216	-0.24127	-0.02148
I	-2.51906	0.12855	0.01667
H	2.57970	1.80673	-0.36273
H	4.33118	2.05027	-0.65428
H	3.72246	1.94203	0.99367

H	5.25164	-1.47692	0.27728
H	5.76235	0.14264	0.85254
H	5.71513	-0.19505	-0.87269

6.4 Acetophenone

SCF energy:	–384.782411 hartree
Zero-point correction:	+0.138631 hartree
Enthalpy correction:	+0.147391 hartree
Free energy correction:	+0.105710 hartree
Quasiharmonic free energy correction:	+0.106429 hartree

Cartesian Coordinates

C	1.69637	-0.20421	-0.00007
C	2.53900	1.04702	0.00025
C	0.20304	-0.06322	-0.00004
O	2.20976	-1.30398	-0.00027
C	-0.42011	1.18689	-0.00016
C	-1.80863	1.27636	-0.00012
C	-2.58013	0.11847	0.00003
C	-1.96379	-1.13230	0.00015
C	-0.57903	-1.22192	0.00010
H	-0.08366	-2.18517	0.00019
H	-3.66148	0.18905	0.00005
H	-2.56519	-2.03336	0.00029
H	0.16944	2.09565	-0.00023
H	-2.28640	2.24847	-0.00022
H	3.58992	0.76756	-0.00010
H	2.31966	1.65302	0.88223
H	2.31929	1.65403	-0.88091

6.5 Acetophenone-Iodine Complex

SCF energy:	–975.751262 hartree
Zero-point correction:	+0.139826 hartree
Enthalpy correction:	+0.153273 hartree
Free energy correction:	+0.094011 hartree
Quasiharmonic free energy correction:	+0.099484 hartree

Cartesian Coordinates

C	-2.49114	0.56097	-0.00013
C	-2.15482	2.02790	-0.00012
C	-3.92723	0.14748	-0.00003
O	-1.61631	-0.28835	-0.00024
C	-4.96063	1.08779	0.00011
C	-6.28624	0.66729	0.00021
C	-6.58444	-0.69192	0.00017
C	-5.55707	-1.63464	0.00003
C	-4.23421	-1.21694	-0.00006
H	-3.42405	-1.93573	-0.00017
H	-7.61770	-1.01836	0.00025
H	-5.79102	-2.69226	0.00000
H	-4.74082	2.14831	0.00014
H	-7.08428	1.39948	0.00032
I	1.15813	-0.11984	-0.00008

I	3.84186	-0.03978	0.00009
H	-1.07447	2.15500	-0.00021
H	-2.58111	2.51148	0.88157
H	-2.58127	2.51153	-0.88170

6.6 Benzophenone

SCF energy:	–576.460566 hartree
Zero-point correction:	+0.192585 hartree
Enthalpy correction:	+0.204229 hartree
Free energy correction:	+0.155073 hartree
Quasiharmonic free energy correction:	+0.156247 hartree

Cartesian Coordinates

C	-0.00004	1.11495	0.00015
C	1.29244	0.36068	0.03146
C	-1.29245	0.36065	-0.03138
O	-0.00007	2.33059	0.00033
C	1.41216	-0.87280	0.67619
C	2.64838	-1.50770	0.73844
C	3.76182	-0.92472	0.14050
C	3.64582	0.30490	-0.50582
C	2.41804	0.95144	-0.54889
C	-1.41195	-0.87300	-0.67577
C	-2.64812	-1.50804	-0.73812
C	-3.76174	-0.92493	-0.14072
C	-3.64600	0.30496	0.50521
C	-2.41831	0.95157	0.54843
H	-2.31444	1.91451	1.03421
H	-4.72147	-1.42643	-0.18109
H	-4.51340	0.75840	0.96944
H	-0.54764	-1.32598	-1.14709
H	-2.74087	-2.45709	-1.25193
H	0.54799	-1.32565	1.14789
H	2.74139	-2.45659	1.25250
H	2.31402	1.91420	-1.03501
H	4.72158	-1.42617	0.18079
H	4.51307	0.75828	-0.97040

6.7 Benzophenone-Iodine Complex

SCF energy:	–1167.430819 hartree
Zero-point correction:	+0.193628 hartree
Enthalpy correction:	+0.210008 hartree
Free energy correction:	+0.143701 hartree
Quasiharmonic free energy correction:	+0.149970 hartree

Cartesian Coordinates

C	2.20485	-0.15784	-0.41655
C	2.00625	1.30200	-0.18315
C	3.52021	-0.78723	-0.10712
O	1.29173	-0.83824	-0.85999
C	2.56684	1.94811	0.92144
C	2.29646	3.29318	1.14781
C	1.48975	4.00022	0.26058

C	0.93668	3.36075	-0.84738
C	1.18277	2.01136	-1.06174
C	4.71471	-0.06437	-0.16917
C	5.92552	-0.70349	0.07433
C	5.94553	-2.05727	0.39691
C	4.75574	-2.78136	0.46083
C	3.54765	-2.15162	0.19797
H	2.61467	-2.70121	0.23256
H	6.88942	-2.55084	0.59597
H	4.77394	-3.83482	0.71204
H	4.70129	0.98743	-0.42881
H	6.85155	-0.14529	0.01198
H	3.19150	1.39599	1.61397
H	2.71628	3.78864	2.01459
H	0.75074	1.49871	-1.91351
H	1.28975	5.05109	0.43303
H	0.31173	3.91316	-1.53836
I	-1.44388	-0.50344	-0.30129
I	-4.04636	-0.32621	0.32200

6.8 Benzaldehyde

SCF energy:	–345.476038 hartree
Zero-point correction:	+0.110566 hartree
Enthalpy correction:	+0.117840 hartree
Free energy correction:	+0.079949 hartree
Quasiharmonic free energy correction:	+0.079949 hartree

Cartesian Coordinates

C	-1.98680	0.46670	0.00006
C	-0.53018	0.20569	0.00003
O	-2.83463	-0.39443	-0.00011
C	0.35132	1.28655	-0.00001
C	1.72421	1.06282	-0.00002
C	2.20900	-0.24180	-0.00003
C	1.32787	-1.32509	0.00000
C	-0.04105	-1.10370	0.00007
H	-0.04014	2.29880	-0.00003
H	2.41221	1.89921	-0.00004
H	-0.74329	-1.92923	0.00013
H	3.27813	-0.41871	-0.00006
H	1.71501	-2.33675	-0.00000
H	-2.27114	1.53510	0.00029

6.9 Benzaldehyde-Iodine Complex

SCF energy:	–936.444154 hartree
Zero-point correction:	+0.111850 hartree
Enthalpy correction:	+0.123755 hartree
Free energy correction:	+0.068494 hartree
Quasiharmonic free energy correction:	+0.072875 hartree

Cartesian Coordinates

C	2.43239	-0.25083	-0.00011
C	3.90325	-0.18754	-0.00002

O	1.70901	0.72444	-0.00017
C	4.62875	-1.37963	-0.00005
C	6.01865	-1.34359	0.00002
C	6.67499	-0.11622	0.00012
C	5.95008	1.07748	0.00015
C	4.56443	1.04483	0.00008
H	3.98099	1.95798	0.00011
H	7.75822	-0.08610	0.00018
H	6.47125	2.02686	0.00023
H	4.10333	-2.32897	-0.00012
H	6.58716	-2.26516	0.00000
I	-1.03868	0.29169	-0.00007
I	-3.67084	-0.23323	0.00007
H	1.99641	-1.26561	-0.00009

6.10 Methyl Acetate

SCF energy:	–268.329276 hartree
Zero-point correction:	+0.090451 hartree
Enthalpy correction:	+0.097498 hartree
Free energy correction:	+0.060623 hartree
Quasiharmonic free energy correction:	+0.061357 hartree

Cartesian Coordinates

C	-1.79610	-0.51280	0.00005
C	-0.46039	0.17167	-0.00015
O	0.54457	-0.71291	-0.00005
C	1.86676	-0.16256	0.00005
H	2.54078	-1.01424	0.00010
H	2.02136	0.44703	-0.88982
H	2.02124	0.44704	0.88993
O	-0.28200	1.36421	0.00002
H	-2.58763	0.23147	0.00006
H	-1.87890	-1.14972	0.88152
H	-1.87907	-1.14989	-0.88128

6.11 Methyl-Acetate-Iodine Complex

SCF energy:	–859.296747 hartree
Zero-point correction:	+0.091684 hartree
Enthalpy correction:	+0.103351 hartree
Free energy correction:	+0.048631 hartree
Quasiharmonic free energy correction:	+0.053162 hartree

Cartesian Coordinates

C	3.26072	1.92411	0.00095
C	3.50506	0.44591	-0.00226
O	4.80137	0.15230	0.01689
C	5.13844	-1.24272	0.01562
H	6.22335	-1.28092	0.03292
H	4.72207	-1.72849	0.89715
H	4.75084	-1.71993	-0.88354
O	2.64750	-0.41150	-0.02013
I	-0.13758	-0.16229	-0.00884
I	-2.81255	0.03364	0.00673

H	2.19248	2.12441	-0.01547
H	3.74026	2.37070	-0.87087
H	3.71168	2.36242	0.89200

7 Intramolecular Aza-Michael Reaction

7.1 Aminochalcone (11)

SCF energy:	–709.193374 hartree
Zero-point correction:	+0.242961 hartree
Enthalpy correction:	+0.258302 hartree
Free energy correction:	+0.199679 hartree
Quasiharmonic free energy correction:	+0.202846 hartree

Cartesian Coordinates

C	-3.30116	2.16494	-0.41170
C	-4.54607	1.57310	-0.16447
C	-4.64261	0.22775	0.11849
C	-3.49680	-0.59554	0.16608
C	-2.22581	0.00359	-0.05182
C	-2.16859	1.37891	-0.34570
H	-3.22694	3.21747	-0.65135
H	-5.44838	2.17278	-0.20222
H	-5.61142	-0.22470	0.30022
H	-1.20907	1.83402	-0.55461
N	-3.64655	-1.91787	0.46604
H	-2.87762	-2.53965	0.26901
H	-4.57871	-2.29910	0.46653
C	-0.98774	-0.80530	-0.00405
O	-1.01875	-2.03246	-0.04915
C	0.31912	-0.10419	0.11883
C	1.45695	-0.76660	-0.12503
H	0.32661	0.93377	0.42263
C	2.82194	-0.23823	-0.02886
H	1.37078	-1.80440	-0.43846
C	3.88137	-1.04072	-0.46851
C	5.19423	-0.58603	-0.40797
C	5.46715	0.67952	0.10027
C	4.42120	1.48633	0.54923
C	3.11164	1.03337	0.48633
H	3.66830	-2.02835	-0.86325
H	6.00152	-1.21944	-0.75542
H	6.48857	1.03723	0.15133
H	4.63066	2.47006	0.95205
H	2.31258	1.66971	0.84777

7.2 Iodine

SCF energy:	–590.956970 hartree
Zero-point correction:	+0.000530 hartree
Enthalpy correction:	+0.004346 hartree
Free energy correction:	–0.025153 hartree
Quasiharmonic free energy correction:	–0.025153 hartree

Cartesian Coordinates

I	0.00000	0.00000	1.33114
I	0.00000	0.00000	-1.33114

7.3 Aminochalcone-Iodine Complex 11–I_2

SCF energy:	–1300.164877 hartree
Zero-point correction:	+0.244087 hartree
Enthalpy correction:	+0.264159 hartree
Free energy correction:	+0.188435 hartree
Quasiharmonic free energy correction:	+0.197291 hartree

Cartesian Coordinates

C	5.92382	-0.52845	-0.63416
C	6.10793	-1.91788	-0.57435
C	5.07722	-2.75160	-0.20480
C	3.80234	-2.23934	0.12869
C	3.59755	-0.83325	0.03768
C	4.68198	-0.01249	-0.33544
H	6.74091	0.12577	-0.90775
H	7.07464	-2.34598	-0.81385
H	4.54260	1.06051	-0.36482
H	5.23212	-3.82364	-0.15216
N	2.81926	-3.10823	0.48167
C	2.29052	-0.23571	0.34549
O	1.40541	-0.88689	0.91489
C	2.02236	1.16738	-0.05095
C	1.05026	1.85599	0.56262
H	2.60820	1.60068	-0.85060
C	0.61533	3.22550	0.27508
H	0.51485	1.35560	1.36603
C	-0.47426	3.73849	0.98887
C	-0.31855	5.82148	-0.20747
C	0.77039	5.32294	-0.92339
C	1.23379	4.03738	-0.68619
C	-0.94052	5.02637	0.74919
H	-0.95871	3.11619	1.73383
H	-1.78651	5.40733	1.30834
H	-0.67715	6.82627	-0.39634
H	2.08220	3.66675	-1.24903
H	1.25783	5.94125	-1.66760
I	-1.30177	-0.98873	0.26401
H	3.05615	-4.07754	0.61511
H	1.97469	-2.75003	0.89858
I	-3.89221	-1.22469	-0.39676

7.4 Transition State TS1

SCF energy:	–709.144133 hartree
Zero-point correction:	+0.243791 hartree
Enthalpy correction:	+0.257631 hartree
Free energy correction:	+0.203676 hartree
Quasiharmonic free energy correction: +	0.205147 hartree
Imaginary Frequency:	498.11 *i*cm^{-1}

Cartesian Coordinates

C	4.28339	-0.65826	0.40199
C	3.76532	-1.82514	-0.14676

C	2.44786	-1.85654	-0.59861
C	1.65206	-0.72546	-0.48201
C	2.15724	0.46119	0.07210
C	3.48160	0.47543	0.49791
H	3.87130	1.40092	0.90516
H	5.30874	-0.62904	0.74990
H	4.37989	-2.71322	-0.22893
H	2.04044	-2.76012	-1.03812
N	0.25954	-0.77523	-0.88628
C	1.33495	1.74216	0.14281
C	-0.06162	1.56972	0.20928
C	-0.59766	0.27052	0.41088
H	-0.07590	-1.73346	-0.97669
C	-2.05532	0.03166	0.24846
H	-0.15894	-0.34333	1.19780
C	-2.79100	0.69619	-0.73742
C	-4.15164	0.45300	-0.87927
C	-4.79155	-0.45408	-0.03676
C	-2.70077	-0.88768	1.07851
C	-4.06491	-1.12363	0.94340
H	-2.29394	1.39986	-1.39587
H	-2.13183	-1.41141	1.83946
H	-4.55860	-1.82988	1.59996
H	-4.71438	0.97062	-1.64682
H	-5.85336	-0.63970	-0.14676
H	-0.71136	2.40083	-0.03050
O	1.94338	2.82181	0.04829
H	0.08640	-0.27441	-1.75813

7.5 Transition State TS1–I_2

SCF energy:	–1300.126417 hartree
Zero-point correction:	+0.245023 hartree
Enthalpy correction:	+0.263469 hartree
Free energy correction:	+0.193900 hartree
Quasiharmonic free energy correction:	+0.199213 hartree
Imaginary Frequency:	472.20 *i*cm^{-1}

Cartesian Coordinates

C	3.39787	-4.23671	-0.52101
C	4.62019	-3.79888	-0.02814
C	2.30397	-3.37621	-0.51216
C	2.41912	-2.07350	-0.03719
C	3.66156	-1.64361	0.46217
C	4.74970	-2.50466	0.47266
H	3.29298	-5.24345	-0.90570
H	5.47864	-4.45932	-0.02663
H	1.33791	-3.70306	-0.87759
H	5.69956	-2.16477	0.86977
N	3.81198	-0.27832	0.90685
C	1.19749	-1.18813	-0.00288
O	0.09539	-1.77269	0.18629
C	1.39804	0.19346	-0.07975
C	2.68554	0.68736	-0.38799
H	4.78929	-0.00183	0.97350

H	0.61020	0.86746	0.22833
I	-2.07297	-0.64147	0.06776
C	3.01258	2.11981	-0.24092
H	3.24534	0.19088	-1.17759
C	3.95044	2.69856	-1.10062
C	4.27180	4.04613	-0.98610
C	3.67090	4.82047	0.00219
C	2.74711	4.24661	0.87421
C	2.41730	2.90314	0.75351
H	4.41973	2.09027	-1.86646
H	2.28517	4.84774	1.64787
H	1.70423	2.45708	1.43757
H	4.99059	4.49025	-1.66380
H	3.92352	5.86989	0.09609
H	3.34648	-0.09375	1.79459
I	-4.56085	0.52108	-0.07485

7.6 Zwitterion 22

SCF energy: –709.152337 hartree
Zero-point correction: +0.246595 hartree
Enthalpy correction: +0.260338 hartree
Free energy correction: +0.206464 hartree
Quasiharmonic free energy correction: +0.208370 hartree

Cartesian Coordinates

C	-2.82942	1.82493	-0.76804
C	-2.17519	2.50766	0.25376
C	-1.31827	1.81817	1.10816
C	-1.13658	0.46310	0.90113
C	-1.76574	-0.24985	-0.11443
C	-2.62859	0.45932	-0.94685
H	-3.13214	-0.08812	-1.73425
H	-3.49894	2.36189	-1.42930
H	-2.32894	3.57039	0.39152
H	-0.80702	2.32896	1.91656
N	-0.25634	-0.30332	1.79729
C	-1.50699	-1.72813	-0.32667
C	-0.37120	-2.21404	0.28821
C	0.57943	-1.33236	1.03044
H	-0.82953	-0.82358	2.47109
C	1.63327	-0.55094	0.24959
H	1.09079	-1.89461	1.81483
C	1.49663	-0.29216	-1.11251
C	2.46092	0.45455	-1.78339
C	3.57205	0.94119	-1.10073
C	2.75540	-0.06817	0.92731
C	3.72114	0.67623	0.25800
H	0.64000	-0.68839	-1.64506
H	2.88314	-0.28521	1.98467
H	4.59050	1.03993	0.79257
H	2.34605	0.65142	-2.84265
H	4.32424	1.51669	-1.62709
H	-0.07801	-3.24660	0.14911
O	-2.33427	-2.36388	-1.04121
H	0.34743	0.33446	2.32268

7.7 Zwitterion 22–I_2

SCF energy:	–1300.144304 hartree
Zero-point correction:	+0.249180 hartree
Enthalpy correction:	+0.267253 hartree
Free energy correction:	+0.198382 hartree
Quasiharmonic free energy correction:	+0.203807 hartree

Cartesian Coordinates

C	-3.57074	-3.27542	-1.14273
C	-4.70739	-2.92124	-0.42288
C	-2.35293	-2.64784	-0.89768
C	-2.25557	-1.65226	0.07162
C	-3.40796	-1.33142	0.78330
C	-4.62888	-1.93750	0.56037
H	-3.63410	-4.04392	-1.90323
H	-5.65471	-3.40691	-0.61859
H	-1.46256	-2.91174	-1.45363
H	-5.50272	-1.65532	1.13638
N	-3.26592	-0.31304	1.83500
C	-0.98273	-0.91118	0.32081
O	0.08508	-1.50252	-0.14514
C	-1.06574	0.28244	0.95947
C	-2.38001	0.85314	1.39888
H	-2.83089	-0.73965	2.66172
H	-0.19201	0.89886	1.11786
I	2.10945	-0.52919	-0.06639
C	-3.16096	1.68915	0.39658
H	-2.24920	1.43916	2.30986
C	-4.06125	2.64112	0.87922
C	-4.82602	3.39901	-0.00101
C	-4.69203	3.20981	-1.37349
C	-3.78833	2.26942	-1.85996
C	-3.02127	1.51319	-0.97937
H	-4.15480	2.80049	1.94942
H	-3.67441	2.12768	-2.92785
H	-2.30418	0.79629	-1.36148
H	-5.51595	4.14047	0.38319
H	-5.28286	3.80143	-2.06249
H	-4.18698	0.03305	2.11838
I	4.72521	0.60181	-0.03157

7.8 Enol Product 23

SCF energy:	–709.188121 hartree
Zero-point correction:	+0.245258 hartree
Enthalpy correction:	+0.259447 hartree
Free energy correction:	+0.203834 hartree
Quasiharmonic free energy correction:	+0.206822 hartree

Cartesian Coordinates

C	-4.36259	-0.50878	0.14644
C	-3.80493	-1.78399	0.07427
C	-2.43024	-1.95378	-0.03664

C	-1.58386	-0.84114	-0.07983
C	-2.14550	0.44845	-0.00486
C	-3.52568	0.60147	0.11086
H	-3.93480	1.60237	0.17412
H	-5.43439	-0.38220	0.23151
H	-4.44525	-2.65812	0.10136
H	-2.00218	-2.94911	-0.08793
N	-0.20483	-0.97987	-0.11519
C	-1.21741	1.58260	-0.02037
C	0.07430	1.42000	-0.32468
C	0.61557	0.06620	-0.72520
H	0.11280	-1.91548	-0.33284
C	2.06105	-0.09671	-0.28888
H	0.59376	-0.01793	-1.82471
C	3.08528	-0.09753	-1.23169
C	4.41582	-0.21093	-0.83044
C	4.72693	-0.32887	0.51940
C	2.37926	-0.21403	1.06551
C	3.70428	-0.33153	1.46773
H	2.84255	-0.01105	-2.28595
H	1.57884	-0.21597	1.79734
H	3.94243	-0.42415	2.52099
H	5.20502	-0.21185	-1.57310
H	5.75990	-0.42052	0.83377
H	0.75554	2.26358	-0.35636
O	-1.79423	2.77633	0.29207
H	-1.14039	3.48026	0.22184

7.9 Michael Product 12

SCF energy:	–709.210590 hartree
Zero-point correction:	+0.245511 hartree
Enthalpy correction:	+0.259499 hartree
Free energy correction:	+0.204723 hartree
Quasiharmonic free energy correction:	+0.206781 hartree

Cartesian Coordinates

C	4.39942	-0.54601	0.08867
C	3.78706	-1.80371	0.18742
C	2.41175	-1.93180	0.17585
C	1.59342	-0.79304	0.06284
C	2.20574	0.47197	-0.04391
C	3.60369	0.57600	-0.02761
H	4.03813	1.56501	-0.11673
H	5.47827	-0.46038	0.10033
H	4.39863	-2.69401	0.27944
H	1.94887	-2.90888	0.25863
N	0.21832	-0.92056	0.03420
C	1.37626	1.68046	-0.23760
O	1.84944	2.79803	-0.30941
C	-0.10954	1.43779	-0.40024
C	-0.58047	0.23821	0.42389
H	-0.29247	1.23292	-1.46269
H	-0.65461	2.34146	-0.12680
H	-0.12725	-1.80212	0.39260
C	-2.05400	-0.02775	0.21590

H	-0.41360	0.46534	1.48755
C	-2.97844	0.38712	1.17299
C	-4.34215	0.19373	0.96834
C	-4.79107	-0.42335	-0.19495
C	-2.50990	-0.64569	-0.95027
C	-3.87145	-0.84428	-1.15306
H	-2.62946	0.86267	2.08386
H	-1.79373	-0.97375	-1.69579
H	-4.21547	-1.32752	-2.05996
H	-5.05141	0.51977	1.71986
H	-5.85152	-0.57874	-0.35394

8 Intermolecular Aza-Michael Reaction

8.1 Methyl Acrylate (13)

SCF energy:	–306.396654 hartree
Zero-point correction:	+0.096104 hartree
Enthalpy correction:	+0.103613 hartree
Free energy correction:	+0.065748 hartree
Quasiharmonic free energy correction:	+0.065937 hartree

Cartesian Coordinates

C	2.48062	-0.00620	-0.00006
C	1.31781	-0.64750	0.00002
C	0.04111	0.11152	0.00012
H	3.42060	-0.54362	-0.00012
H	2.51101	1.07787	-0.00005
H	1.24466	-1.72802	0.00001
O	-0.06031	1.31456	0.00001
O	-1.01088	-0.71383	0.00003
C	-2.29866	-0.08709	-0.00006
H	-2.41563	0.53073	0.88988
H	-3.02092	-0.89798	-0.00016
H	-2.41548	0.53081	-0.88997

8.2 Methyl Acrylate Iodine Complex (13–I_2)

SCF energy:	–897.363601 hartree
Zero-point correction:	+0.097313 hartree
Enthalpy correction:	+0.109510 hartree
Free energy correction:	+0.053023 hartree
Quasiharmonic free energy correction:	+0.057934 hartree

Cartesian Coordinates

C	4.15128	2.42355	0.01109
C	3.15110	1.54886	-0.01259
H	5.18418	2.09747	0.03498
H	3.95599	3.48889	0.00720
H	2.11264	1.85782	-0.03628
C	3.35194	0.08218	-0.00776
O	4.62570	-0.29027	0.01378
C	4.87324	-1.70313	0.02106
H	5.95362	-1.80916	0.03850
H	4.42734	-2.15580	0.90582
H	4.45573	-2.16001	-0.87527
O	2.43650	-0.71738	-0.02211
I	-0.33182	-0.26620	-0.00914
I	-2.98427	0.12721	0.00765

8.3 Methyl Acrylate Iodine Complex with Double Bond

SCF energy:	–897.361878 hartree
Zero-point correction:	+0.097231 hartree
Enthalpy correction:	+0.109407 hartree
Free energy correction:	+0.053567 hartree
Quasiharmonic free energy correction:	+0.057990 hartree

Cartesian Coordinates

C	2.67428	-2.23521	0.17654
C	2.99277	-1.14937	-0.52573
C	3.32736	0.12398	0.16921
H	2.42809	-3.16972	-0.31241
H	2.66098	-2.20398	1.26106
H	3.02432	-1.14162	-1.60878
O	3.34617	0.27870	1.36560
O	3.59810	1.09265	-0.70735
C	3.91096	2.37397	-0.14680
H	3.06919	2.73915	0.44104
H	4.09945	3.02732	-0.99329
H	4.79444	2.30013	0.48651
I	-0.20762	-0.57020	-0.10515
I	-2.68035	0.43430	0.05648

8.4 Pyrrolidine (14)

SCF energy:	–212.505399 hartree
Zero-point correction:	+0.130540 hartree
Enthalpy correction:	+0.136396 hartree
Free energy correction:	+0.102457 hartree
Quasiharmonic free energy correction:	+0.102742 hartree

Cartesian Coordinates

C	0.77525	-1.02646	-0.05768
C	-0.77600	-1.02587	-0.05783
C	-1.15504	0.44518	0.17472
H	-1.19463	-1.67313	0.71309
H	-1.15715	-1.36629	-1.02140
C	1.15538	0.44438	0.17461
N	0.00039	1.16916	-0.36420
H	-1.28371	0.63021	1.25198
H	-2.07369	0.73749	-0.33575
H	0.00075	2.14008	-0.06971
H	1.15636	-1.36746	-1.02105
H	1.19321	-1.67381	0.71353
H	1.28439	0.62946	1.25180
H	2.07416	0.73595	-0.33607

8.5 Transition State TS2

SCF energy:	–518.893674 hartree
Zero-point correction:	+0.229364 hartree
Enthalpy correction:	+0.241863 hartree
Free energy correction:	+0.189926 hartree
Quasiharmonic free energy correction:	+0.192504 hartree
Imaginary Frequency:	268.19 *i*cm^{-1}

Cartesian Coordinates

C	2.96079	-1.21111	0.11279
C	3.71265	0.10147	-0.13681
C	1.67639	-1.00398	-0.68320
H	2.72825	-1.32668	1.17495
H	3.51402	-2.09098	-0.21325
N	1.34769	0.40485	-0.41079
H	1.84921	-1.16156	-1.75147
H	0.83780	-1.62950	-0.36581
C	2.59789	1.15979	-0.15030
H	2.50060	1.65744	0.82028
H	2.75403	1.92741	-0.90775
H	4.20252	0.06421	-1.11230
H	4.47069	0.31415	0.61626
C	0.14738	0.51742	1.11279
C	-0.96819	-0.29435	0.99152
H	0.02358	1.58731	0.97001
H	0.91178	0.24747	1.83587
C	-2.07615	0.16652	0.21330
O	-2.14577	1.22022	-0.41136
O	-3.12040	-0.71098	0.20781
C	-4.25572	-0.32138	-0.55740
H	-3.98851	-0.18179	-1.60581
H	-4.68305	0.60599	-0.17392
H	-4.97422	-1.13195	-0.45940
H	-0.99793	-1.29423	1.40086
H	0.77661	0.81857	-1.14083

8.6 Transition State TS2–I_2

SCF energy:	–1109.870364 hartree
Zero-point correction:	+0.230488 hartree
Enthalpy correction:	+0.247602 hartree
Free energy correction:	+0.179944 hartree
Quasiharmonic free energy correction:	+0.186247 hartree
Imaginary Frequency:	241.41 *i*cm^{-1}

Cartesian Coordinates

C	3.19729	-2.39823	1.34256
C	3.29651	-3.47216	0.24769
C	1.93925	-1.63095	0.95210
H	4.05704	-1.72374	1.30320
H	3.13799	-2.81825	2.34578
N	2.06743	-1.55474	-0.50581

H	1.03047	-2.17055	1.23897
H	1.89644	-0.61835	1.36309
C	2.66570	-2.81488	-0.99857
H	3.40463	-2.57926	-1.76953
H	1.90444	-3.45262	-1.45056
H	2.71542	-4.34981	0.53565
H	4.32119	-3.79457	0.06633
C	3.26007	0.01398	-0.96373
C	3.24142	1.01385	-0.01371
H	2.72783	0.17245	-1.89566
H	4.13265	-0.62662	-1.03167
C	2.24898	2.03600	-0.07923
O	1.33781	2.12070	-0.91359
O	2.36902	2.96776	0.89105
C	1.40223	4.01797	0.88235
H	0.39413	3.61458	0.98629
H	1.46629	4.59163	-0.04243
H	1.64422	4.64820	1.73422
H	3.93503	1.02771	0.81596
H	1.18782	-1.33024	-0.96086
I	-0.89270	0.73543	-0.36312
I	-3.06185	-0.75446	0.21719

8.7 Zwitterion 24

SCF energy:	–518.902097 hartree
Zero-point correction:	+0.231758 hartree
Enthalpy correction:	+0.243803 hartree
Free energy correction:	+0.194068 hartree
Quasiharmonic free energy correction:	+0.195506 hartree

Cartesian Coordinates

C	2.86108	1.20983	-0.35573
C	3.30916	-0.24781	-0.48905
C	1.33554	1.10908	-0.38252
H	3.23520	1.85306	-1.15069
H	3.19681	1.61646	0.60123
N	1.02425	-0.25584	0.17623
H	0.82227	1.85846	0.21672
H	0.94329	1.14732	-1.39876
C	2.31943	-0.96536	0.41758
H	2.18988	-2.02719	0.21587
H	2.58015	-0.82813	1.46955
H	4.33965	-0.41522	-0.17900
H	3.19608	-0.59159	-1.52021
C	0.09120	-0.25019	1.36533
C	-1.27689	0.16372	0.93801
H	0.52283	0.41637	2.11477
H	0.14435	-1.27738	1.74605
C	-1.76713	-0.42563	-0.20477
O	-1.11433	-1.25187	-0.92212
O	-3.01588	-0.13775	-0.69802
C	-3.83147	0.75266	0.04007
H	-4.78063	0.81155	-0.48892
H	-3.38259	1.74888	0.09117
H	-4.00108	0.38174	1.05462

H	-1.80095	0.91837	1.49979
H	0.42123	-0.78274	-0.51820

8.8 Zwitterion 24–I_2

SCF energy:	–1109.884323 hartree
Zero-point correction:	+0.234133 hartree
Enthalpy correction:	+0.250973 hartree
Free energy correction:	+0.185745 hartree
Quasiharmonic free energy correction:	+0.189778 hartree

Cartesian Coordinates

C	0.84289	-2.89146	-0.85211
C	1.21910	-3.37411	0.57269
C	1.88091	-1.81840	-1.20841
H	-0.16299	-2.47116	-0.86348
H	0.87694	-3.70061	-1.57971
N	2.47605	-1.42828	0.10880
H	2.70207	-2.21697	-1.80681
H	1.47748	-0.93387	-1.69405
C	2.56197	-2.70986	0.86884
H	2.74868	-2.49915	1.91992
H	3.40231	-3.26786	0.45134
H	1.29194	-4.45744	0.64648
H	0.47477	-3.03708	1.29583
C	3.74912	-0.62174	0.02949
C	3.51787	0.69350	-0.63352
C	2.54199	1.51316	-0.15877
O	1.78763	1.24076	0.85797
O	2.31909	2.68373	-0.83067
C	1.70453	3.72872	-0.08298
H	0.68200	3.47482	0.19787
H	1.69806	4.59693	-0.73862
H	2.28125	3.95124	0.81754
H	4.11907	0.98789	-1.48007
H	4.07641	-0.53178	1.06995
H	4.47265	-1.23308	-0.51083
H	1.81227	-0.80709	0.59360
I	-0.51436	0.66890	0.36385
I	-3.07525	-0.22308	-0.18480

8.9 Enol Product 25

SCF energy:	–518.903604 hartree
Zero-point correction:	+0.230957 hartree
Enthalpy correction:	+0.243104 hartree
Free energy correction:	+0.193255 hartree
Quasiharmonic free energy correction:	+0.194391 hartree

Cartesian Coordinates

C	3.30948	0.34308	-0.38740
C	2.62152	1.16659	0.73280
C	1.38627	0.34135	1.10796

H	2.32004	2.14511	0.35690
H	3.26967	1.32723	1.59397
N	1.07744	-0.39117	-0.12735
H	0.53384	0.94475	1.42284
H	1.62095	-0.37350	1.91251
C	2.38344	-0.86196	-0.59941
H	2.31899	-1.19013	-1.63782
H	2.71291	-1.71582	0.01353
H	4.31451	0.02392	-0.11237
H	3.38708	0.93067	-1.30262
C	0.09661	-1.46875	0.04769
C	-1.29939	-0.93800	0.26997
H	0.39112	-2.11346	0.88914
H	0.13993	-2.08649	-0.85727
C	-1.72244	0.17895	-0.34827
O	-2.94779	0.73121	-0.26940
C	-3.91620	0.03775	0.50069
O	-0.95346	0.93366	-1.14550
H	-0.01815	0.60167	-1.00394
H	-4.07412	-0.96931	0.10673
H	-4.83439	0.61382	0.42148
H	-3.60693	-0.02240	1.54729
H	-1.96326	-1.49086	0.91614

8.10 Michael Product 15

SCF energy:	–518.935844 hartree
Zero-point correction:	+0.231201 hartree
Enthalpy correction:	+0.243729 hartree
Free energy correction:	+0.192192 hartree
Quasiharmonic free energy correction:	+0.194270 hartree

Cartesian Coordinates

C	2.87540	1.12920	0.19373
C	2.62133	0.43071	-1.16712
C	2.00325	0.34735	1.18093
H	2.55690	2.17146	0.15326
H	3.92565	1.11227	0.48498
N	0.91202	-0.15951	0.35126
C	1.58112	-0.65450	-0.85303
H	3.52824	-0.00248	-1.58912
H	2.22350	1.13939	-1.89404
H	2.07904	-1.61827	-0.64352
H	0.86754	-0.80698	-1.66429
H	1.61450	0.95469	2.00062
H	2.57588	-0.49128	1.61583
C	0.10213	-1.15271	1.03374
C	-1.08431	-1.59091	0.17211
H	0.69805	-2.04225	1.30165
H	-0.27024	-0.70847	1.95958
C	-1.81485	-0.38617	-0.36163
H	-1.77158	-2.18839	0.77492
H	-0.76192	-2.18858	-0.67970
O	-1.93697	-0.10496	-1.52848
O	-2.32211	0.36048	0.62527
C	-2.97748	1.56774	0.22362

H	-2.27825	2.21297	-0.30800
H	-3.31187	2.04272	1.14147
H	-3.82650	1.34128	-0.42090

8.11 Cationic Hypoiodite 28

SCF energy:	–814.186318 hartree
Zero-point correction:	+0.235565 hartree
Enthalpy correction:	+0.249553 hartree
Free energy correction:	+0.192427 hartree
Quasiharmonic free energy correction:	+0.195519 hartree

Cartesian Coordinates

C	-1.55300	0.54783	-1.29374
C	-0.62929	1.58864	-0.74958
C	0.44203	1.21067	-0.03168
O	0.56744	-0.08953	0.30590
O	1.40648	1.97035	0.47414
C	1.40172	3.35372	0.11774
H	2.30896	3.77293	0.54176
H	0.52683	3.84814	0.54367
H	1.40546	3.46113	-0.96843
I	2.36966	-0.96934	0.04848
H	-0.85089	2.63381	-0.90299
N	-2.30060	-0.17301	-0.19914
H	-1.01948	-0.22989	-1.84345
H	-2.30939	0.98559	-1.94350
C	-3.20114	0.72188	0.64142
C	-4.54469	-0.01243	0.71739
C	-4.19859	-1.46785	0.38754
C	-3.15058	-1.31139	-0.70026
H	-3.26144	1.69289	0.15455
H	-2.72811	0.84373	1.61339
H	-5.23126	0.38578	-0.03135
H	-5.00283	0.10512	1.69744
H	-5.05564	-2.04207	0.04046
H	-3.77021	-1.97526	1.25523
H	-3.59597	-0.98512	-1.64159
H	-2.51458	-2.17651	-0.87591
H	-1.57924	-0.56737	0.41202

8.12 Iodide Anion

SCF energy:	–295.644810 hartree
Zero-point correction:	+0.000000 hartree
Enthalpy correction:	+0.002360 hartree
Free energy correction:	–0.016848 hartree
Quasiharmonic free energy correction:	–0.016848 hartree

Cartesian Coordinates

I	0.00000	0.00000	0.00000

8.13 Hypoiodite 29

SCF energy:	–813.730928 hartree
Zero-point correction:	+0.219644 hartree
Enthalpy correction:	+0.233664 hartree
Free energy correction:	+0.176072 hartree
Quasiharmonic free energy correction:	+0.179534 hartree

Cartesian Coordinates

C	1.60592	1.09272	-1.12240
C	0.51655	1.84674	-0.41969
C	-0.75718	1.43854	-0.37804
O	-1.18463	0.37100	-1.08911
O	-1.77825	2.01181	0.28935
C	-1.45960	3.08400	1.16607
H	-0.70839	2.77073	1.89534
H	-2.38517	3.34465	1.67230
H	-1.09167	3.94536	0.60369
I	-1.92988	-1.16004	0.00181
H	0.79144	2.76635	0.08046
N	2.58107	0.56525	-0.17382
H	2.13636	1.76811	-1.80096
H	1.17680	0.28134	-1.73144
C	3.73459	-0.04311	-0.83510
C	4.43827	-0.80894	0.29183
C	3.30022	-1.13250	1.29521
C	2.04978	-0.51580	0.65587
H	4.35909	0.71952	-1.30450
H	3.39976	-0.74395	-1.62092
H	5.19572	-0.18073	0.76203
H	4.93436	-1.70461	-0.08245
H	3.49981	-0.67140	2.26320
H	3.17705	-2.20355	1.45699
H	1.32723	-0.13724	1.38082
H	1.53549	-1.26157	0.02159

8.14 Hydrogen Iodide

SCF energy:	–296.066614 hartree
Zero-point correction:	+0.005346 hartree
Enthalpy correction:	+0.008651 hartree
Free energy correction:	–0.014786 hartree
Quasiharmonic free energy correction:	–0.014786 hartree

Cartesian Coordinates

I	0.00000	0.00000	0.02988
H	0.00000	0.00000	-1.58368

8.15 N-Iodo-Pyrrolidinium Cation 32

SCF energy:	–507.794797 hartree
Zero-point correction:	+0.134030 hartree

Enthalpy correction: +0.141263 hartree
Free energy correction: +0.100839 hartree
Quasiharmonic free energy correction: +0.102179 hartree

Cartesian Coordinates

C	1.49131	-1.18236	0.58452
N	0.62682	0.00271	0.93442
C	1.49202	1.18539	0.57784
C	2.13441	0.77274	-0.74688
H	2.22545	1.26053	1.38256
H	0.89074	2.09007	0.54730
C	2.12859	-0.77869	-0.74492
H	0.89028	-2.08745	0.56238
H	2.22743	-1.25107	1.38749
I	-1.20480	-0.00003	-0.10516
H	1.54521	-1.16417	-1.58042
H	3.13040	-1.19707	-0.81613
H	3.14009	1.18288	-0.81201
H	1.56030	1.16062	-1.58759
H	0.37858	0.00565	1.92571

8.16 N-Iodo-Pyrrolidine 33

SCF energy: –507.360846 hartree
Zero-point correction: +0.119691 hartree
Enthalpy correction: +0.126635 hartree
Free energy correction: +0.088024 hartree
Quasiharmonic free energy correction: +0.088024 hartree

Cartesian Coordinates

C	-1.44326	-1.14865	-0.61176
N	-0.60376	-0.00003	-1.01205
C	-1.44330	1.14858	-0.61185
C	-2.12199	0.77470	0.71956
H	-2.19302	1.24147	-1.40594
H	-0.86465	2.06979	-0.58307
C	-2.12203	-0.77463	0.71957
H	-0.86452	-2.06979	-0.58284
H	-2.19290	-1.24167	-1.40591
I	1.17880	0.00001	0.09592
H	-1.54882	-1.16293	1.56271
H	-3.12710	-1.19229	0.77980
H	-3.12702	1.19244	0.77988
H	-1.54862	1.16296	1.56259

9 Friedel-Crafts Reaction

9.1 *trans*-Crotonophenone (16)

SCF energy:	–462.153221 hartree
Zero-point correction:	+0.172288 hartree
Enthalpy correction:	+0.183349 hartree
Free energy correction:	+0.135763 hartree
Quasiharmonic free energy correction:	+0.137021 hartree

Cartesian Coordinates

C	3.03848	0.72487	0.22218
C	1.71252	1.13209	0.18065
C	3.35887	-0.62045	0.04485
C	2.35025	-1.55438	-0.16990
C	1.01910	-1.14952	-0.19418
C	0.69234	0.19754	-0.02036
C	-0.72162	0.69302	-0.07381
H	3.82357	1.45224	0.39008
H	1.44684	2.17459	0.30717
H	4.39431	-0.93879	0.07244
H	2.59827	-2.59834	-0.31818
H	0.24522	-1.88563	-0.37360
O	-0.94552	1.86935	-0.29865
C	-1.81912	-0.27795	0.16854
C	-3.09089	0.05735	-0.06210
H	-1.57168	-1.26198	0.54988
C	-4.26408	-0.83511	0.16349
H	-3.28949	1.05630	-0.44444
H	-4.81462	-0.97914	-0.77019
H	-4.95959	-0.37059	0.86799
H	-3.96368	-1.80832	0.55192

9.2 *trans*-Crotonophenone Iodine Complex (16–I_2)

SCF energy:	–1053.123503 hartree
Zero-point correction:	+0.173505 hartree
Enthalpy correction:	+0.189154 hartree
Free energy correction:	+0.125345 hartree
Quasiharmonic free energy correction:	+0.130497 hartree

Cartesian Coordinates

C	1.87732	2.70980	1.08237
C	1.92432	1.32293	1.13476
C	2.46246	3.38512	0.01307
C	3.10145	2.67349	-0.99822
C	3.17263	1.28574	-0.93556
C	2.58170	0.60593	0.13180
C	2.56943	-0.88674	0.20218
H	1.38071	3.26408	1.86943
H	1.46178	0.78498	1.95443
H	2.41694	4.46670	-0.03306
H	3.54429	3.19801	-1.83608

H	3.66284	0.73034	-1.72635
O	1.55300	-1.47113	0.55975
C	3.77220	-1.66644	-0.13679
C	5.01442	-1.17086	-0.13270
H	3.59436	-2.72436	-0.30697
C	6.24220	-1.97794	-0.38899
H	5.16393	-0.11700	0.08836
H	6.90663	-1.93637	0.47825
H	6.79850	-1.55674	-1.23078
H	6.00338	-3.01908	-0.60463
I	-1.07761	-0.61886	0.19562
I	-3.63307	0.07155	-0.25151

9.3 Indole (17)

SCF energy: –363.707520 hartree
Zero-point correction: +0.130689 hartree
Enthalpy correction: +0.137834 hartree
Free energy correction: +0.100437 hartree
Quasiharmonic free energy correction: +0.100437 hartree

Cartesian Coordinates

C	-2.15316	0.69014	0.00003
C	-0.98259	1.42640	0.00003
C	-2.12730	-0.71965	0.00001
C	-0.93195	-1.41635	-0.00001
C	0.24913	-0.66744	-0.00002
C	0.24813	0.74898	0.00000
C	1.62316	1.16595	0.00001
N	1.56129	-1.07657	-0.00004
C	2.38055	0.02853	-0.00001
H	3.45256	-0.09024	-0.00002
H	1.99837	2.17705	0.00002
H	-3.10880	1.20083	0.00005
H	-1.01158	2.51026	0.00005
H	-3.06205	-1.26760	0.00002
H	-0.90995	-2.49986	-0.00002
H	1.87664	-2.03384	-0.00007

9.4 Transition State TS3

SCF energy: –825.827928 hartree
Zero-point correction: +0.304981 hartree
Enthalpy correction: +0.322321 hartree
Free energy correction: +0.259780 hartree
Quasiharmonic free energy correction: +0.262897 hartree
Imaginary Frequency: 460.21 $i$cm^{-1}

Cartesian Coordinates

C	-5.06285	-1.41485	0.20169
C	-3.69805	-1.29779	-0.04009
C	-5.86077	-0.27507	0.26464
C	-5.28373	0.97969	0.08245

C	-3.91697	1.09432	-0.15096
C	-3.10657	-0.04351	-0.20744
C	-1.62133	0.02920	-0.45651
H	-5.50580	-2.39483	0.33807
H	-3.06797	-2.17690	-0.10339
H	-6.92538	-0.36351	0.44713
H	-5.90099	1.87010	0.11497
H	-3.48234	2.07431	-0.31040
O	-1.04116	-1.00008	-0.90292
C	-0.92391	1.19500	-0.12950
C	0.48536	1.26069	-0.37695
H	-1.40507	2.01067	0.39591
C	1.09499	2.64766	-0.34295
H	0.62958	3.24440	-1.13109
H	2.16822	2.63731	-0.52391
H	0.89611	3.14163	0.61125
C	3.04251	-1.09151	0.05721
C	2.85283	0.21105	0.54015
C	3.93240	1.09326	0.52693
C	5.14726	0.65648	0.00998
C	5.29617	-0.64016	-0.49888
C	4.24046	-1.54293	-0.48003
H	6.25261	-0.94921	-0.90214
H	4.34876	-2.55320	-0.85472
H	3.83548	2.09569	0.92623
H	5.99616	1.32915	0.00328
C	0.93726	-1.00699	0.83076
N	1.84789	-1.79213	0.27266
H	-0.02681	-1.39120	1.11597
H	1.68442	-2.75381	0.00590
H	0.80686	0.66097	-1.22820
C	1.43608	0.33324	0.93965
H	1.14326	0.93725	1.78894

9.5 Transition State TS3–I_2

SCF energy:	–1416.814051 hartree
Zero-point correction:	+0.306324 hartree
Enthalpy correction:	+0.328235 hartree
Free energy correction:	+0.250698 hartree
Quasiharmonic free energy correction:	+0.257813 hartree
Imaginary Frequency:	477.47 *i*cm^{-1}

Cartesian Coordinates

C	0.20419	4.21237	1.78455
C	0.83640	3.23604	1.02173
C	-0.99268	4.77462	1.34855
C	-1.55984	4.35048	0.14896
C	-0.93347	3.36798	-0.60802
C	0.27585	2.80759	-0.18551
C	0.91304	1.75263	-1.03364
H	0.64250	4.52867	2.72373
H	1.75797	2.79194	1.38055
H	-1.48422	5.53516	1.94371
H	-2.49225	4.78351	-0.19364

H	-1.37135	3.02459	-1.53795
O	0.14888	1.03091	-1.77441
C	2.28562	1.57075	-1.00944
C	2.90273	0.54400	-1.78982
C	4.41047	0.54736	-1.84294
H	4.83841	0.39270	-0.84809
H	4.74215	1.52801	-2.19294
H	4.80714	-0.20834	-2.52049
C	3.90082	-1.93197	0.49571
C	2.77101	-1.10709	0.40918
C	2.34380	-0.41385	1.54095
C	3.06631	-0.56753	2.71823
C	4.19851	-1.39381	2.77704
C	4.63826	-2.09453	1.66160
H	4.73752	-1.49194	3.71120
H	5.50887	-2.73708	1.69898
H	1.46199	0.21518	1.50318
H	2.74813	-0.04463	3.61203
C	3.15055	-2.08217	-1.61049
N	4.09149	-2.50326	-0.77082
H	3.13202	-2.41910	-2.63716
H	4.84957	-3.12605	-1.01878
H	2.40741	0.33471	-2.73398
C	2.32326	-1.11766	-0.98327
H	1.29014	-0.97882	-1.28181
H	2.90449	2.15722	-0.34191
I	-1.64082	-0.21544	-0.68922
I	-3.61806	-1.74195	0.48666

9.6 Wheland Intermediate 26

SCF energy:	–825.826500 hartree
Zero-point correction:	+0.305514 hartree
Enthalpy correction:	+0.323155 hartree
Free energy correction:	+0.259407 hartree
Quasiharmonic free energy correction:	+0.263345 hartree

Cartesian Coordinates

C	4.52368	0.71095	1.20429
C	3.33977	-0.01662	1.14101
C	5.14291	1.14755	0.03459
C	4.57173	0.84095	-1.19765
C	3.39064	0.10688	-1.25747
C	2.75110	-0.32129	-0.09126
C	1.46139	-1.09706	-0.21499
H	4.96948	0.93067	2.16787
H	2.87965	-0.36790	2.05742
H	6.06584	1.71361	0.08451
H	5.04950	1.17115	-2.11331
H	2.94232	-0.14944	-2.20989
O	1.21795	-1.66373	-1.33348
C	0.57501	-1.10619	0.84451
C	-0.73707	-1.76644	0.68019
H	0.73231	-0.48787	1.71952
C	-1.58522	-1.75544	1.94518
H	-2.54681	-2.25696	1.80678

H	-1.77403	-0.73062	2.27663
H	-1.04817	-2.27041	2.74438
C	-3.33988	0.41613	-0.33108
C	-1.94491	0.36080	-0.29537
C	-1.23459	1.51950	-0.00016
C	-1.95233	2.68555	0.25604
C	-3.35114	2.70818	0.21675
C	-4.07897	1.56141	-0.08187
H	-3.87679	3.63314	0.41832
H	-5.16111	1.56520	-0.11877
H	-0.15224	1.50768	0.02703
H	-1.41717	3.59828	0.48833
C	-2.79295	-1.70229	-0.82438
N	-3.79747	-0.88288	-0.65743
H	-2.95835	-2.74409	-1.06579
H	-4.77373	-1.14639	-0.73776
H	-0.61626	-2.78776	0.30593
C	-1.52297	-1.04192	-0.56499
H	-0.77302	-1.19225	-1.36143

9.7 Wheland Intermediate 26–I_2

SCF energy:	–1416.825532 hartree
Zero-point correction:	+0.309056 hartree
Enthalpy correction:	+0.330723 hartree
Free energy correction:	+0.254963 hartree
Quasiharmonic free energy correction:	+0.260721 hartree

Cartesian Coordinates

C	-0.84132	3.67686	2.09888
C	-1.34479	2.65898	1.29379
C	0.21004	4.46959	1.64740
C	0.75899	4.23716	0.38773
C	0.25929	3.21751	-0.41358
C	-0.80410	2.42452	0.02763
C	-1.33943	1.34989	-0.86033
H	-1.26341	3.84361	3.08307
H	-2.15068	2.02788	1.65291
H	0.60428	5.25997	2.27516
H	1.57834	4.85053	0.03142
H	0.68726	3.02996	-1.39207
O	-0.46426	0.62576	-1.55662
C	-2.67466	1.17747	-0.98915
C	-3.31755	0.14749	-1.87797
C	-2.91249	0.23973	-3.35235
H	-1.83699	0.11096	-3.47350
H	-3.17526	1.22689	-3.73600
H	-3.43664	-0.51089	-3.94950
C	-2.47378	-1.84765	0.86456
C	-3.56850	-1.49319	0.08367
C	-4.79781	-1.30045	0.69102
C	-4.88622	-1.48225	2.07212
C	-3.76981	-1.84006	2.83018
C	-2.52507	-2.03114	2.23340
H	-3.86939	-1.97000	3.90040
H	-1.65029	-2.30272	2.81006

H	-5.66930	-1.01447	0.11420
H	-5.83897	-1.34083	2.56716
C	-1.66980	-1.68993	-1.23531
N	-1.35700	-1.96825	-0.01071
H	-0.94477	-1.75937	-2.03262
H	-0.41231	-2.20481	0.28612
H	-4.40026	0.28432	-1.81733
C	-3.10579	-1.31666	-1.33686
H	-3.60001	-2.00036	-2.03710
H	-3.32786	1.84431	-0.44012
I	1.47491	-0.07451	-0.63285
I	3.89746	-1.13663	0.43845

9.8 Product 18

SCF energy:	–825.901297 hartree
Zero-point correction:	+0.307665 hartree
Enthalpy correction:	+0.325101 hartree
Free energy correction:	+0.263827 hartree
Quasiharmonic free energy correction:	+0.265842 hartree

Cartesian Coordinates

C	1.44334	1.81814	-1.92040
C	0.22053	1.79000	-1.25644
C	2.63077	1.82240	-1.19583
C	2.59637	1.81497	0.19817
C	1.37729	1.79669	0.85993
C	0.17819	1.77581	0.13970
C	-1.10150	1.67761	0.91723
H	1.46673	1.82972	-3.00355
H	-0.69064	1.77292	-1.83927
H	3.58234	1.83129	-1.71455
H	3.51997	1.81407	0.76464
H	1.33432	1.77214	1.94179
O	-1.09936	1.85558	2.12031
C	-2.38945	1.27293	0.23000
C	-2.58413	-0.26704	0.27146
C	-3.90812	-0.63048	-0.40049
H	-3.90030	-0.33866	-1.45435
H	-4.74069	-0.11470	0.08244
H	-4.08509	-1.70602	-0.34590
C	0.69858	-1.84670	-0.63382
C	-0.20448	-1.36442	0.34304
C	0.20040	-1.32678	1.68720
C	1.47187	-1.76108	2.01482
C	2.35773	-2.23313	1.02443
C	1.98672	-2.28386	-0.30784
H	3.34943	-2.56149	1.31257
H	2.66689	-2.64472	-1.07045
H	-0.46712	-0.94838	2.45425
H	1.79936	-1.73413	3.04738
C	-1.19970	-1.25181	-1.66823
N	0.06314	-1.77148	-1.84818
H	0.44885	-2.06703	-2.73055
H	-2.63749	-0.55350	1.32754
C	-1.40963	-0.97714	-0.34364

H	-1.84935	-1.10500	-2.51778
H	-2.42501	1.60349	-0.80898
H	-3.20790	1.74905	0.77385

9.9 Cationic Hypoiodite 30

SCF energy:	–1121.134440 hartree
Zero-point correction:	+0.309170 hartree
Enthalpy correction:	+0.328516 hartree
Free energy correction:	+0.258347 hartree
Quasiharmonic free energy correction:	+0.264498 hartree

Cartesian Coordinates

C	-2.79194	2.32277	1.68920
C	-1.84773	1.41022	1.23376
C	-3.37542	3.22498	0.80341
C	-3.01496	3.20799	-0.54175
C	-2.07218	2.29547	-1.00051
C	-1.47352	1.39668	-0.11353
C	-0.44818	0.43248	-0.57367
H	-3.07212	2.33028	2.73568
H	-1.38865	0.70835	1.92096
H	-4.11458	3.93329	1.15794
H	-3.47904	3.89710	-1.23700
H	-1.81545	2.26469	-2.05330
O	-0.35669	-0.74324	0.12430
C	0.43812	0.66972	-1.54901
C	1.45740	-0.32470	-2.03042
H	0.44184	1.65611	-2.00524
C	1.63563	-0.25537	-3.54696
H	0.68424	-0.46277	-4.03854
H	2.36666	-0.99055	-3.88753
H	1.96607	0.73547	-3.86974
C	3.10477	0.83451	0.84101
C	2.77601	-0.34953	0.19047
C	2.45372	-1.46616	0.94356
C	2.47764	-1.34847	2.33219
C	2.80836	-0.14304	2.95761
C	3.13347	0.98839	2.21500
H	2.81369	-0.08624	4.03863
H	3.39390	1.92834	2.68381
H	2.18040	-2.40101	0.46978
H	2.23003	-2.20838	2.94197
C	3.26948	1.30836	-1.35379
N	3.39545	1.79797	-0.16777
H	3.45568	1.91156	-2.23316
H	3.67113	2.75853	0.02536
H	1.13766	-1.32958	-1.74473
C	2.82577	-0.11373	-1.29444
I	-1.94533	-1.98280	-0.00276
H	3.57753	-0.73977	-1.79144

9.10 Hypoiodite 31

SCF energy:	–1120.720277 hartree
Zero-point correction:	+0.296079 hartree
Enthalpy correction:	+0.315456 hartree
Free energy correction:	+0.245751 hartree
Quasiharmonic free energy correction:	+0.251336 hartree

Cartesian Coordinates

C	2.55135	-3.33841	0.75826
C	1.61556	-2.43397	0.27043
C	3.91129	-3.11819	0.55226
C	4.33120	-1.98683	-0.14239
C	3.39664	-1.08331	-0.63554
C	2.02916	-1.30529	-0.44428
C	1.04220	-0.33918	-0.97668
H	2.21993	-4.20796	1.31327
H	0.55956	-2.59038	0.46087
H	4.64012	-3.82059	0.93879
H	5.38805	-1.80841	-0.30152
H	3.72018	-0.20356	-1.18006
O	1.47803	0.95698	-1.11924
C	-0.19539	-0.64878	-1.38106
C	-1.22549	0.35453	-1.82811
H	-0.47816	-1.69712	-1.41130
C	-1.28376	0.42374	-3.35927
H	-2.02761	1.15482	-3.68437
H	-1.54779	-0.55032	-3.77980
H	-0.31120	0.71623	-3.75706
C	-4.19600	-0.46206	0.32405
C	-2.82850	-0.12454	0.18919
C	-2.04089	0.01165	1.34414
C	-2.62817	-0.18789	2.58127
C	-3.99258	-0.52386	2.69229
C	-4.79332	-0.66518	1.57206
H	-4.42336	-0.67485	3.67508
H	-5.84233	-0.92344	1.65762
H	-0.98926	0.26719	1.26501
H	-2.03365	-0.08631	3.48144
C	-3.73909	-0.24871	-1.86193
N	-4.72558	-0.53056	-0.94121
H	-3.96560	-0.25423	-2.91695
H	-5.68302	-0.74808	-1.16632
H	-0.91472	1.33699	-1.45515
C	-2.55858	0.00997	-1.22063
I	1.82207	1.96502	0.59997

9.11 N-Iodo Indolium Cation 34

SCF energy:	–658.946539 hartree
Zero-point correction:	+0.132863 hartree
Enthalpy correction:	+0.141615 hartree
Free energy correction:	+0.098214 hartree
Quasiharmonic free energy correction:	+0.098421 hartree

Cartesian Coordinates

C	-1.06201	-0.06530	0.43112
C	-1.88306	0.90934	-0.12581
C	-3.15779	0.55563	-0.54978
C	-3.55438	-0.77095	-0.39341
C	-2.70641	-1.72404	0.17377
C	-1.42264	-1.38347	0.60078
H	-3.04469	-2.74640	0.28170
H	-0.75197	-2.11669	1.03179
H	-3.82339	1.29143	-0.98241
H	-4.54279	-1.07091	-0.71808
C	0.04549	1.98940	0.43944
N	0.21056	0.56729	0.79552
C	-1.15522	2.17947	-0.10355
I	1.89272	-0.29631	-0.18868
H	-1.53055	3.12765	-0.45894
H	0.87120	2.65087	0.64557
H	0.41009	0.45701	1.79629

9.12 N-Iodo Indole (35)

SCF energy:	–658.552308 hartree
Zero-point correction:	+0.119380 hartree
Enthalpy correction:	+0.128155 hartree
Free energy correction:	+0.084518 hartree
Quasiharmonic free energy correction:	+0.085090 hartree

Cartesian Coordinates

C	1.03442	-0.06932	0.00026
C	2.06146	0.90616	-0.00005
C	3.39888	0.47914	-0.00027
C	3.67115	-0.87683	-0.00021
C	2.63138	-1.82759	0.00008
C	1.30275	-1.44024	0.00033
H	2.87616	-2.88295	0.00012
H	0.50084	-2.16939	0.00056
H	4.20325	1.20603	-0.00051
H	4.69921	-1.21856	-0.00041
C	0.07643	1.96966	0.00023
N	-0.16796	0.60792	0.00054
C	1.42264	2.19242	-0.00008
I	-1.99721	-0.24558	-0.00010
H	1.90151	3.15895	-0.00023
H	-0.74747	2.66615	0.00034

9.13 3-Iodo-Indolium Cation (36)

SCF:	–658.992259 hartree
Zero-point correction:	+0.133290 hartree
Enthalpy correction:	+0.142043 hartree
Free energy correction:	+0.098474 hartree
Quasiharmonic free energy correction:	+0.098836 hartree

Cartesian Coordinates

C	2.87236	-1.63313	0.13816
C	1.60379	-1.41642	0.67403
C	3.57658	-0.61270	-0.50570
C	3.04173	0.66691	-0.63289
C	1.78569	0.85385	-0.08884
C	1.06099	-0.14802	0.55325
C	-0.24381	0.43615	0.97994
N	1.00050	2.04074	-0.04602
C	-0.12213	1.85356	0.56475
H	-0.84643	2.64331	0.71116
I	-1.90293	-0.30136	-0.21480
H	3.32118	-2.61492	0.21926
H	1.05806	-2.21465	1.16155
H	4.55827	-0.81718	-0.91314
H	3.57951	1.46747	-1.12353
H	1.28285	2.92770	-0.45780
H	-0.55290	0.29409	2.01297

9.14 3-Iodo-Indole (37)

SCF:	–658.582006 hartree
Zero-point correction:	+0.120374 hartree
Enthalpy correction:	+0.129152 hartree
Free energy correction:	+0.085908 hartree
Quasiharmonic free energy correction:	+0.085908 hartree

Cartesian Coordinates

C	-2.72450	-1.84241	-0.00001
C	-1.38757	-1.49167	-0.00001
C	-3.73515	-0.85893	0.00001
C	-3.42950	0.48999	0.00003
C	-2.07645	0.84382	0.00003
C	-1.04997	-0.13067	0.00001
C	0.18597	0.59598	0.00001
N	-1.47663	2.08096	0.00005
C	-0.11156	1.92956	0.00005
H	0.54407	2.78549	0.00006
I	2.08146	-0.23539	-0.00002
H	-3.00531	-2.88861	-0.00003
H	-0.60894	-2.24650	-0.00003
H	-4.77373	-1.16715	0.00001
H	-4.20677	1.24491	0.00005
H	-1.95771	2.96695	0.00006

10 Michael Addition to Nitrostyrene

10.1 Nitrostyrene (19)

SCF energy:	–514.029456 hartree
Zero-point correction:	+0.137762 hartree
Enthalpy correction:	+0.147796 hartree
Free energy correction:	+0.101987 hartree
Quasiharmonic free energy correction:	+0.103027 hartree

Cartesian Coordinates

C	-3.07533	1.06333	0.00016
C	-1.70014	1.26553	0.00030
C	-3.58446	-0.23080	-0.00013
C	-2.71565	-1.32295	-0.00022
C	-1.34413	-1.12352	-0.00006
C	-0.81975	0.17735	0.00019
C	0.61551	0.45392	0.00030
C	1.58776	-0.45769	-0.00050
H	0.91378	1.49809	0.00084
N	2.97657	-0.03357	-0.00020
H	1.49789	-1.53244	-0.00103
O	3.24817	1.15211	-0.00076
O	3.81017	-0.92250	0.00091
H	-3.74597	1.91370	0.00027
H	-1.29983	2.27330	0.00054
H	-4.65569	-0.39253	-0.00024
H	-3.11237	-2.33076	-0.00040
H	-0.68336	-1.98213	-0.00001

10.2 Nitrostyrene Iodine Complex (19–I_2)

SCF energy:	–1104.994933 hartree
Zero-point correction:	+0.138623 hartree
Enthalpy correction:	+0.153454 hartree
Free energy correction:	+0.089679 hartree
Quasiharmonic free energy correction:	+0.096328 hartree

Cartesian Coordinates

C	5.14844	-0.21090	-0.00680
C	3.69231	-0.10691	0.01496
C	2.99165	1.02846	0.02791
H	3.13306	-1.03769	0.02533
N	1.54573	0.98369	0.04893
H	3.35934	2.04233	0.02676
O	0.97252	-0.09800	0.05282
O	0.96458	2.05057	0.06151
I	-1.90482	-0.04526	0.01803
C	5.71814	-1.48909	0.03355
C	5.98955	0.91018	-0.06635
C	7.36572	0.74894	-0.08244
C	7.92333	-0.52977	-0.03947
C	7.09867	-1.64817	0.01836

H	5.07167	-2.35849	0.07799
H	5.57173	1.90912	-0.10344
H	8.00858	1.61926	-0.12951
H	8.99994	-0.64998	-0.05262
H	7.52823	-2.64174	0.05066
I	-4.57737	-0.21145	-0.02842

10.3 N-Methyl Pyrrole (20)

SCF energy: –249.397127 hartree
Zero-point correction: +0.111134 hartree
Enthalpy correction: +0.117596 hartree
Free energy correction: +0.082116 hartree
Quasiharmonic free energy correction: +0.082313 hartree

Cartesian Coordinates

C	-0.17225	-1.11487	-0.01175
C	-1.48898	-0.71111	0.01297
C	-1.48898	0.71110	0.01297
H	-2.34890	-1.36244	0.01949
C	-0.17226	1.11488	-0.01175
H	-2.34890	1.36243	0.01949
N	0.61991	0.00000	-0.03251
H	0.26749	-2.09999	-0.02106
H	0.26748	2.10000	-0.02105
C	2.07219	0.00000	0.02210
H	2.45054	0.88592	-0.48578
H	2.45055	-0.88584	-0.48592
H	2.42401	-0.00008	1.05518

10.4 Transition State TS4

SCF energy: –763.405076 hartree
Zero-point correction: +0.250216 hartree
Enthalpy correction: +0.265896 hartree
Free energy correction: +0.207177 hartree
Quasiharmonic free energy correction: +0.209171 hartree
Imaginary Frequency: 479.14 *i*cm^{-1}

Cartesian Coordinates

C	-0.74594	-0.82511	-0.35526
C	0.68062	-0.41004	-0.40431
C	1.68363	-1.29527	0.08443
N	2.98429	-1.02304	-0.18039
O	3.88117	-1.79744	0.22928
O	3.28404	0.01715	-0.82504
C	-1.62354	-0.35784	-1.33556
C	-1.24649	-1.64921	0.65885
C	-2.58569	-2.01210	0.67617
C	-3.45196	-1.54713	-0.31316
C	-2.96957	-0.71710	-1.31758
H	-1.24888	0.27892	-2.13059
H	-0.58959	-1.99959	1.44717
H	-2.95802	-2.65449	1.46509

H	-4.49744	-1.83085	-0.29650
H	-3.63478	-0.35083	-2.09019
C	0.23434	0.97033	1.83532
C	-0.99065	1.59033	1.89496
C	0.81406	1.22701	0.55220
N	-0.06630	2.13337	-0.07068
C	-1.14750	2.29690	0.68186
C	0.19644	2.76848	-1.35290
H	0.50707	2.01976	-2.08216
H	-0.71257	3.25585	-1.69842
H	0.99244	3.50461	-1.24165
H	-1.98074	2.89193	0.33593
H	-1.72344	1.53789	2.68381
H	0.66743	0.30371	2.56668
H	1.87350	1.37072	0.35810
H	0.95995	0.04933	-1.34987
H	1.51102	-2.14243	0.72612

10.5 Transition State TS4–I_2

SCF energy:	–1354.382770 hartree
Zero-point correction:	+0.252076 hartree
Enthalpy correction:	+0.272095 hartree
Free energy correction:	+0.198688 hartree
Quasiharmonic free energy correction:	+0.204823 hartree
Imaginary Frequency:	447.36 *i*cm^{-1}

Cartesian Coordinates

C	-3.83427	-0.25422	-0.49916
C	-2.91624	0.88841	-0.19775
C	-1.63811	0.93038	-0.81033
N	-1.00141	2.12215	-0.94092
O	0.14769	2.15608	-1.48615
O	-1.52327	3.17529	-0.54208
C	-5.16861	-0.16774	-0.08620
C	-3.41965	-1.39826	-1.18532
C	-4.31060	-2.43954	-1.42662
C	-5.62935	-2.35091	-0.99340
C	-6.05948	-1.20518	-0.32782
H	-5.51137	0.72506	0.42795
H	-2.40229	-1.48840	-1.54481
H	-3.97144	-3.31980	-1.95939
H	-6.32072	-3.16323	-1.18221
H	-7.08870	-1.11826	-0.00120
C	-1.93985	1.96701	2.01822
C	-0.62104	1.59872	2.11392
C	-2.70379	0.78626	1.72843
N	-1.81416	-0.29032	1.90643
C	-0.58152	0.18899	2.01836
C	-2.16928	-1.70358	1.82568
H	-1.78246	-2.21896	2.70353
H	-1.75330	-2.14922	0.92178
H	-3.25344	-1.79188	1.80110
H	0.27165	-0.47424	2.05621
H	0.24086	2.23724	2.22545

H	-2.34466	2.96622	2.03651
H	-3.73067	0.63354	2.03237
H	-3.42447	1.84767	-0.19042
H	-1.08423	0.08375	-1.17892
I	2.03920	0.54939	-0.68327
I	3.97626	-1.10194	0.23519

10.6 Wheland Intermediate 27

SCF energy:	–763.407773 hartree
Zero-point correction:	+0.252122 hartree
Enthalpy correction:	+0.267755 hartree
Free energy correction:	+0.209512 hartree
Quasiharmonic free energy correction:	+0.211349 hartree

Cartesian Coordinates

C	-0.90341	-0.75474	-0.21975
C	0.55393	-0.38988	-0.39810
C	1.48392	-1.38362	0.20598
N	2.77349	-1.31748	-0.07969
O	3.20200	-0.39543	-0.86141
O	3.60273	-2.14970	0.41176
C	-1.73922	-0.85298	-1.33301
C	-1.44015	-1.01225	1.04488
C	-2.78279	-1.34217	1.19269
C	-3.61104	-1.42220	0.07577
C	-3.08495	-1.18169	-1.18864
H	-1.33154	-0.69430	-2.32602
H	-0.80438	-0.96876	1.92285
H	-3.18138	-1.54140	2.18033
H	-4.65705	-1.67975	0.19111
H	-3.71706	-1.25620	-2.06547
C	0.63799	1.25497	1.61613
C	-0.19277	2.30487	1.78931
C	0.88428	1.04109	0.17587
N	0.08991	2.09938	-0.43677
C	-0.51596	2.79653	0.47772
C	0.02935	2.31301	-1.87765
H	-0.54993	1.51356	-2.33898
H	1.04245	2.31143	-2.27718
H	-0.44663	3.27098	-2.07199
H	-1.15619	3.62919	0.21535
H	-0.56710	2.72277	2.70985
H	1.08319	0.63458	2.38114
H	1.94399	1.19126	-0.08616
H	0.77681	-0.30612	-1.46724
H	1.16796	-2.16498	0.87760

10.7 Wheland Intermediate 27–I_2

SCF energy:	–1354.390425 hartree
Zero-point correction:	+0.254215 hartree
Enthalpy correction:	+0.274243 hartree

Free energy correction: +0.201135 hartree
Quasiharmonic free energy correction: +0.206957 hartree

Cartesian Coordinates

C	2.82604	-0.95709	-0.56256
C	1.93920	0.24007	-0.29308
C	1.56728	0.96868	-1.54514
N	0.59009	1.84084	-1.53838
O	-0.01870	2.08008	-0.38998
O	0.19732	2.46560	-2.55960
C	2.41716	-2.22526	-0.14808
C	4.04339	-0.82948	-1.23656
C	4.84187	-1.94332	-1.47194
C	4.43269	-3.20198	-1.03866
C	3.21563	-3.34192	-0.38083
H	1.45535	-2.34669	0.33979
H	4.36932	0.14108	-1.59541
H	5.78154	-1.82857	-1.99878
H	5.05510	-4.06925	-1.22330
H	2.88063	-4.31929	-0.05498
C	3.86365	1.86381	0.35825
C	4.78594	1.60429	1.30578
C	2.57109	1.24310	0.73184
N	2.88902	0.60577	2.00782
C	4.13301	0.80981	2.31474
C	1.90511	-0.13276	2.79254
H	2.30071	-0.28951	3.79302
H	1.71103	-1.09422	2.31742
H	0.98542	0.44873	2.84126
H	4.55530	0.41669	3.23095
H	5.81801	1.91337	1.34388
H	3.99399	2.43991	-0.54724
H	1.79984	2.00764	0.90612
H	1.01823	-0.10563	0.18744
H	2.06108	0.80586	-2.49078
I	-1.96372	0.70365	-0.11053
I	-4.16497	-0.93383	0.26719

10.8 Product 21

SCF energy: –763.464825 hartree
Zero-point correction: +0.253704 hartree
Enthalpy correction: +0.269629 hartree
Free energy correction: +0.209399 hartree
Quasiharmonic free energy correction: +0.212791 hartree

Cartesian Coordinates

C	1.32378	-0.40720	0.05940
C	-0.16407	-0.50947	0.37896
C	-0.71108	-1.74694	-0.32542
N	-2.14171	-2.01462	0.06703
O	-2.42961	-1.92850	1.23996
O	-2.91543	-2.32552	-0.81176
C	2.25705	-1.00477	0.90664
C	1.76782	0.25755	-1.08355

C	3.12750	0.32325	-1.37402
C	4.05467	-0.27313	-0.52388
C	3.61671	-0.93802	0.61824
H	1.91745	-1.51788	1.80119
H	1.04596	0.73567	-1.73811
H	3.46251	0.84539	-2.26246
H	5.11326	-0.21594	-0.74750
H	4.33278	-1.39979	1.28766
C	-1.85476	0.92043	-1.02692
C	-2.22200	2.29359	-0.99060
C	-0.93466	0.71435	-0.01873
N	-0.73497	1.91107	0.62227
C	-1.51212	2.87284	0.03404
C	0.18231	2.13555	1.72804
H	-0.00410	1.41771	2.52811
H	0.01691	3.13923	2.11430
H	1.21828	2.04200	1.39678
H	-1.49832	3.88622	0.40327
H	-2.92746	2.79387	-1.63473
H	-0.26809	-0.67544	1.45570
H	-0.70813	-1.65454	-1.40928
H	-0.16491	-2.64202	-0.02496
H	-2.22578	0.17447	-1.71387

11 Decomposition of Iodine

11.1 Iodine

SCF:	–590.956970 hartree
Zero-point correction:	+0.000530 hartree
Enthalpy correction:	+0.004346 hartree
Free energy correction:	–0.025153 hartree
Quasiharmonic free energy correction:	–0.025153 hartree

Cartesian Coordinates

I	0.00000	0.00000	1.33114
I	0.00000	0.00000	-1.33114

11.2 Water

SCF:	–76.424698 hartree
Zero-point correction:	+0.021521 hartree
Enthalpy correction:	+0.025301 hartree
Free energy correction:	+0.003881 hartree
Quasiharmonic free energy correction:	+0.003881 hartree

Cartesian Coordinates

O	0.00000	0.00000	0.11740
H	0.00000	0.76048	-0.46959
H	0.00000	-0.76048	-0.46959

11.3 Hydrogen Iodide (HI)

SCF:	–296.066614 hartree
Zero-point correction:	+0.005346 hartree
Enthalpy correction:	+0.008651 hartree
Free energy correction:	–0.014786 hartree
Quasiharmonic free energy correction:	–0.014786 hartree

Cartesian Coordinates

I	0.00000	0.00000	0.02988
H	0.00000	0.00000	-1.58368

11.4 Hypoiodous Acid (HOI)

SCF:	–371.255624 hartree
Zero-point correction:	+0.012720 hartree
Enthalpy correction:	+0.016669 hartree
Free energy correction:	–0.012226 hartree
Quasiharmonic free energy correction:	–0.012226 hartree

Cartesian Coordinates

O	0.01494	1.69602	0.00000
H	-0.91104	1.96803	0.00000
I	0.01494	-0.29313	-0.00000

12 HI-Catalyzed Friedel-Crafts Reaction

12.1 Protonated *trans*-Crotonophenone (16–H$^+$)

SCF:	–462.564649 hartree
Zero-point correction:	+0.185246 hartree
Enthalpy correction:	+0.196387 hartree
Free energy correction:	+0.149222 hartree
Quasiharmonic free energy correction:	+0.149801 hartree

Cartesian Coordinates

C	-3.00856	0.73135	0.31991
C	-1.68048	1.11555	0.26547
C	-3.35900	-0.59444	0.06630
C	-2.38205	-1.54329	-0.22775
C	-1.04751	-1.17474	-0.26147
C	-0.68894	0.16252	-0.02624
C	0.70442	0.55844	-0.09643
H	-3.77026	1.45890	0.56757
H	-1.42062	2.14116	0.50553
H	-4.40053	-0.88967	0.10334
H	-2.66210	-2.56880	-0.43014
H	-0.29252	-1.90954	-0.50955
O	1.02131	1.78410	-0.38074
C	1.77867	-0.34310	0.16286
C	3.06473	0.02643	-0.03309
H	1.53242	-1.32668	0.53902
C	4.22984	-0.84001	0.23808
H	3.26695	1.02316	-0.41640
H	3.94381	-1.81920	0.61638
H	4.88581	-0.34143	0.95896
H	4.81922	-0.95101	-0.67740
H	0.26069	2.31799	-0.65729

12.2 Transition State TS–H$^+$

SCF:	–826.278964 hartree
Zero-point correction:	+0.317510 hartree
Enthalpy correction:	+0.335413 hartree
Free energy correction:	+0.270784 hartree
Quasiharmonic free energy correction:	+0.274942 hartree
Imaginary Frequency:	266.30 *i*cm^{-1}

Cartesian Coordinates

C	4.28469	0.88560	1.28039
C	3.12462	0.12636	1.24718
C	4.97990	1.15266	0.10253
C	4.51565	0.65637	-1.11215
C	3.35975	-0.11177	-1.15197
C	2.65546	-0.37956	0.02869
C	1.42430	-1.17782	-0.01392
H	4.65208	1.26407	2.22599
H	2.59760	-0.10017	2.16608

H	5.88418	1.74820	0.13231
H	5.04853	0.87305	-2.02934
H	2.99089	-0.46237	-2.11012
O	1.28689	-2.08903	-0.97247
C	0.37079	-0.99539	0.84887
C	-0.76918	-1.81665	0.81010
H	0.39925	-0.15468	1.52952
C	-1.79358	-1.69397	1.88537
H	-2.61675	-2.39303	1.75969
H	-2.18060	-0.67215	1.94585
H	-1.29988	-1.90321	2.84049
C	-3.24370	0.55254	-0.19259
C	-1.93990	0.39056	-0.69626
C	-1.06590	1.48262	-0.69856
C	-1.52374	2.69449	-0.20422
C	-2.83202	2.83281	0.29092
C	-3.71495	1.76376	0.30698
H	-3.15787	3.79469	0.66712
H	-4.72251	1.86411	0.69102
H	-0.05794	1.38453	-1.08576
H	-0.86517	3.55440	-0.20128
C	-3.04310	-1.58688	-0.82978
N	-3.88054	-0.68196	-0.29376
H	-3.36031	-2.60546	-0.99662
H	-4.82694	-0.87506	0.00359
H	-0.68515	-2.76379	0.28957
C	-1.79504	-1.00390	-1.05215
H	-1.01832	-1.43804	-1.66334
H	2.12341	-2.26031	-1.42532

12.3 Protonated Intermediate 26–H$^+$

SCF:	–826.294819 hartree
Zero-point correction:	+0.320336 hartree
Enthalpy correction:	+0.338202 hartree
Free energy correction:	+0.274102 hartree
Quasiharmonic free energy correction:	+0.277978 hartree

Cartesian Coordinates

C	-3.85128	-1.59096	0.01518
C	-2.63690	-1.13080	-0.48268
C	-4.69275	-0.72807	0.71066
C	-4.31593	0.59868	0.90610
C	-3.10367	1.06192	0.40931
C	-2.25021	0.19858	-0.28334
C	-0.94459	0.67057	-0.80196
H	-4.13682	-2.62491	-0.13642
H	-1.97580	-1.81574	-1.00324
H	-5.64054	-1.08564	1.09455
H	-4.97440	1.27768	1.43438
H	-2.82369	2.10098	0.53808
O	-0.53680	0.14708	-1.99483
C	-0.14851	1.52240	-0.14642
C	1.17860	1.99949	-0.66470
H	-0.47295	1.87462	0.82796
C	1.35515	3.50676	-0.47709

H	2.33354	3.83904	-0.82958
H	1.24730	3.79703	0.57134
H	0.58801	4.03566	-1.04399
C	2.14735	-0.90102	1.04180
C	2.27959	-0.28393	-0.19773
C	2.28305	-1.06467	-1.34138
C	2.15841	-2.44562	-1.19216
C	2.02583	-3.03611	0.06727
C	2.01678	-2.26477	1.22623
H	1.92798	-4.11137	0.14556
H	1.91246	-2.70459	2.20954
H	2.36932	-0.61792	-2.32390
H	2.16037	-3.07628	-2.07247
C	2.29818	1.29818	1.49601
N	2.16974	0.12927	2.02534
H	2.33651	2.19028	2.10774
H	2.09876	-0.03899	3.02640
H	1.25144	1.75599	-1.72670
C	2.35105	1.20464	0.01025
H	3.29982	1.63385	-0.33567
H	-1.29595	-0.20279	-2.47452

13 References

(1) (a) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515; (b) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176–2179.

(2) Pitts, M. R.; Harrison, J. R.; Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 955–977.

(3) Banik, B. K.; Fernandez, M.; Alvarez, C. *Tetrahedron Lett.* **2005**, *46*, 2479–2482.

(4) Blay, G.; Fernández, I.; Pedro, J. R.; Vila, C. *Synthesis* **2012**, *44*, 3590–3594.

(5) Banks, J. L.; Beard, H. S.; Cao, Y.; Cho, A. E.; Damm, W.; Farid, R.; Felts, A. K.; Halgren, T. A.; Mainz, D. T.; Maple, J. R.; et al.; *J. Comput. Chem.* **2005**, *26*, 1752–1780.

(6) MacroModel; 10.6, V.; Schrödinger, LLC: New York, NY, 2014.

(7) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(8) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(9) Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2003**, *119*, 11113–11123.

(10) Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032–3041.

(11) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101.

(12) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

(13) Ribeiro, R. F.; Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2011**, *115*, 14556–14562.

(14) Schwabe, T.; Grimme, S. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3397–3406.

(15) Gaussian09, Revision D.01: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al.; Gaussian, Inc.: Wallingford CT, 2009.

(16) NBO 6.0; E. D. Glendening, J., K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold; Theoretical Chemistry Institute, University of Wisconsin: Madison, 2013.

(17) (a) Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W. *J. Am. Chem. Soc.* **2010**, *132*, 6498–6506; (b) Contreras-García, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W. *J. Chem. Theory Comput.* **2011**, *7*, 625–632.