

Supporting Information for

Alkane Dehydrogenation Catalyzed by PN3P Pincer Iridium Hydride Complex

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General Information

All manipulations involving air- and moisture-sensitive compounds were performed under an inert argon atmosphere using standard Schlenk or glovebox techniques. Solvents were purified by distillation over appropriate drying agents and stored under argon prior to use. Unless otherwise noted, commercially available reagents were used as received without further purification. Cyclooctane and tert-butylethylene substrate was obtained from Sigma-Aldrich. Column chromatography was conducted on silica gel (60–120 mesh).

NMR spectra (^1H , ^{13}C) were recorded on Bruker Avance 400MHz spectrometers in deuterated solvents. ^1H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents, and the ^{13}C NMR chemical shifts were referenced to the ^{13}C signals of the deuterated solvents. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, s = sextet, h = heptet, m = multiplet, br = broad), coupling constants (Hz) and integration. Gas chromatography was performed on Agilent 7890B coupled with an Agilent 5977B Mass Spectrometer Detector.

The synthesis PN³P iridium complexes, PN³P^{tBu}IrH₂Cl (**Ir1**), PN³P^{tBu}IrH₂(**Ir2**) and PN³P^{tBu}IrH₃(**Ir3**) were carried out following previously reported procedures.¹ The alkane dehydrogenation reactions employed cyclooctane as substrate and tert-butylethylene as hydrogen acceptor unless otherwise specified.

Abbreviations:

COA: Cyclooctane

TBE: *Tert*-butylethylene

COE: Cyclooctene

Fe: Ferrocene

NaO^tBu: Sodium *tert*-butoxide

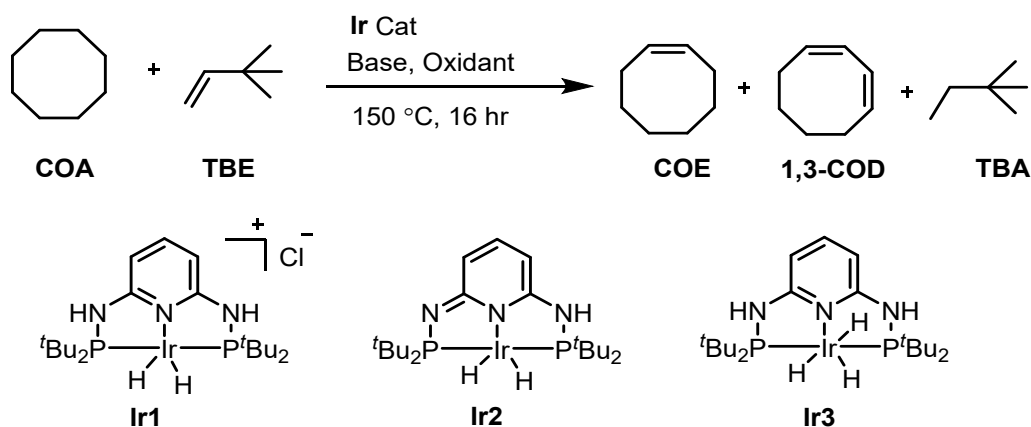
KO^tBu: Potassium *tert*-butoxide

Experimental methods

I. Optimizing reaction conditions for cyclooctane dehydrogenation:

In an argon-filled glovebox, into a J-young NMR tube, COA (3.0 mmol, 0.404 ml) and TBE (3.0 mmol, 0.386 ml) was added followed by the addition of iridium complexes **Ir1**, **Ir2** or **Ir3** (3.0 μ mol) and base (15.0 μ mol). The NMR tube was removed from glovebox and heated at 150°C in an oil bath for 24 hours. The crude reaction mixture was cooled and analyzed by GC-MS using 100 μ l of the crude reaction mixture in MeOH solvent with mesitylene (100 μ l) as internal standard.

Table 1: Optimization of reaction conditions for cyclooctane dehydrogenation^a



Entry	Ir cat.	Base	Oxidant	Conv. (%)	TON ^b
1	Ir1	NaO ^t Bu	-	10	99
2	Ir2	NaO ^t Bu	-	55	546
3	Ir3	NaO ^t Bu	-	40	403
4	Ir1	NaO ^t Bu	Fe	16	157
5	Ir2	NaO ^t Bu	Fe	56	558
6	Ir3	NaO ^t Bu	Fe	42	415
7	Ir2	KO ^t Bu	-	48	481
8	Ir2	KO ^t Bu	Fe	50	502

^aReaction conditions: COA (3.0 mmol, 0.404 mL), TBE (3.0 mmol, 0.386 mL), iridium complexes **Ir1**, **Ir2** or **Ir3** (3.0 μ mol, 0.1 mol%), base (15.0 μ mol, 0.5 mol%) at 150°C for 24 hr. ^bDetermined by GC using mesitylene as an internal standard. TON were calculated based on conversion of TBE determined by GC.

II. Study of the effect of the different ratios of tert-butylethylene (TBE) for cyclooctane dehydrogenation reaction

In an argon-filled glovebox, into a J-young NMR tube, COA (3.0 mmol, 0.404 ml) and TBE with different ratios was added followed by the addition of **Ir2** (3.0 μ mol) and NaO^tBu (15.0 μ mol). The NMR tube was removed from glovebox and heated at 150°C in an oil bath for 24 hours. The crude reaction mixture was cooled and analyzed by GC-MS using 100 μ l of the crude reaction mixture in MeOH with mesitylene (100 μ l) as internal standard.

Table 2: Effect of different TBE ratios for COA dehydrogenation^a

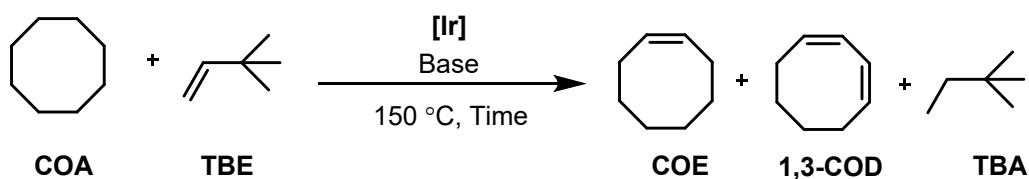
Entry	[Ir]:COA	[Ir]:TBE	Temp.	Conv. (%)	TON ^b
1	1000	100	150	2	3
2	1000	500	150	24	118
3	1000	1000	150	55	546

^aReaction conditions: COA (3.0 mmol, 0.404 mL), TBE (0.3 - 3.0 mmol) **Ir2** (3.0 μ mol, 0.1 mol%), NaO^tBu (15.0 μ mol, 0.5 mol%) at 150°C for 24 hr. ^bDetermined by GC using mesitylene as an internal standard. TON were calculated based on conversion of TBE determined by GC.

III. Study of the effect of reaction time for the dehydrogenation of cyclooctane

In an argon-filled glovebox, into a J-young NMR tube, COA (3.0 mmol, 0.404 ml) and TBE (3.0 mmol, 0.386 ml) was added followed by the addition of **Ir2** (3.0 μ mol) and base (15.0 μ mol). The NMR tube was removed from glovebox and heated at 150°C in an oil bath for 4h, 16h, and 24h. The crude reaction mixture was cooled and analyzed by GC-MS using 100 μ l of the crude reaction mixture in MeOH with mesitylene (100 μ l) as internal standard.

Table 3: Time dependent study of COA dehydrogenation with different bases^a



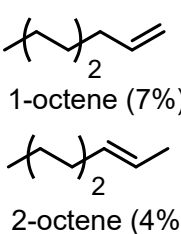
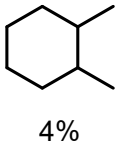



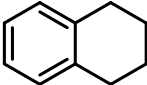
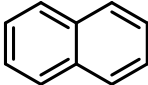
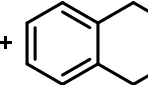
Entry	Time (hr)	Base	Conv. of TBE (%)	TON ^b
1	4	KO ^t Bu	45	447
2	16	KO ^t Bu	47	466
3	24	KO ^t Bu	48	481
4	4	NaO ^t Bu	49	499
5	16	NaO ^t Bu	50	501
6	24	NaO ^t Bu	55	546

^aReaction conditions: COA (3.0 mmol, 0.404 mL), TBE (3.0 mmol, 0.386 mL), **Ir2** (3.0 μ mol, 0.1 mol%), base (15.0 μ mol, 0.5 mol%) at 150°C for specified time shown in the table. ^bDetermined by GC using mesitylene as an internal standard. TON were calculated based on conversion of TBE determined by GC.

IV. Study of the dehydrogenation of different substrates

In an argon-filled glovebox, into a J-young NMR tube, alkane (3.0 mmol) and TBE (3.0 mmol) were added followed by the addition of **Ir2** (3.0 μ mol) and NaO^tBu (15.0 μ mol). The NMR tube was removed from glovebox and heated at 150°C in an oil bath for 24 hours. The crude reaction mixture was cooled and analyzed by GC-MS using 100 μ l of the crude reaction mixture in MeOH with mesitylene (100 μ l) as internal standard.

Table 4: Substrate scope study of dehydrogenation with standard conditions

alkane + TBE		$\xrightarrow[150\text{ }^\circ\text{C, 16 hr}]{\text{Ir2 Cat, NaO}^t\text{Bu}}$		alkene + TBA	
Entry	Alkane	Product		Conv.(%)	
1	n-octane	 1-octene (7%) 2-octene (4%)	 4%	15	
2			 not observed	10	
3		 20%	 5%	25	

^aReaction conditions: Alkane (3.0 mmol), TBE (3.0 mmol), **Ir2** (3.0 μ mol, 0.1 mol%), NaO^tBu (15.0 μ mol, 0.5 mol%) at 150°C for 24 hr. ^bDetermined by GC using mesitylene as an internal standard. TON were calculated based on conversion of TBE determined by GC.

COMPUTATIONAL METHODS

All calculations were performed employing a DFT method implemented in the Gaussian 16 suite of programs.² For geometry optimization and frequency analysis, we adopted the BP86 functional.³ During geometry optimization we used the split-valence plus single polarization basis set def2-SVP⁴ for non-metals and the Stuttgart/Dresden small core RECP (relativistic effective core potential) plus valence double- ζ -basis set (SDD)⁵ for cobalt. The geometries were optimized without any symmetrical constraints. For each transition state, in addition to analyzing the character of the normal mode associated with the imaginary frequency, intrinsic reaction coordinate (IRC) analysis⁶ was performed to confirm that it connects the correct reactant and product on the potential energy surface. To refine the computed energy, single-point calculations were performed using the hybrid-meta-GGA M06 functional⁷ with the def2-TZVP^{3,7} basis set for nonmetals and SDD for Ir. Solvation energies were evaluated implicitly by a self-consistent reaction field (SCRF) approach for all the intermediates and transitions states, using the SMD continuum solvation model.⁸ The free energies (ΔG), calculated at the M06(SMD)/SDD/def2-TZVP//BP86/SDD/def2-SVP level are reported throughout the article unless otherwise mentioned. The ΔG value is obtained by augmenting the in solvent electronic energy (ΔE), calculated at M06(SMD)/SDD/def2-TZVP, with the corresponding free energy corrections calculated at BP86/SDD/def2-SVP in the gas phase.

Table 5. Cartesian coordinates (Å) of the optimized structures of all intermediates and transition states at BP86/SDD(Ir)/Def2-SVP level of theory. E_e^s represents the absolute electronic energy in Hartree at M06/SDD(Ir)/Def2-TZVP level of theory.

Cat.1				C	-13.294927000	14.376231000	16.118467000
$E_e^s = -1776.566893$				C	-13.444385000	15.710545000	15.360842000
				H	-12.823992000	16.517430000	15.797485000
C	-11.276756000	10.989283000	11.414214000	H	-13.168705000	15.592345000	14.293689000
Ir	-11.489376000	11.250062000	16.299910000	H	-14.504167000	16.045471000	15.413034000
P	-11.617596000	13.518071000	15.751370000	C	-14.354938000	13.382946000	15.585590000
N	-11.553266000	13.529238000	14.046384000	H	-14.245717000	13.225357000	14.493283000
C	-11.446535000	12.345684000	13.451519000	H	-14.273745000	12.396086000	16.087569000
N	-11.392358000	11.135123000	14.196406000	H	-15.371412000	13.793344000	15.774881000
C	-11.286456000	9.913833000	13.572685000	C	-13.495549000	14.572732000	17.633381000
C	-11.227014000	9.795814000	12.179147000	H	-13.322186000	13.631881000	18.195962000
C	-11.382289000	12.231980000	12.015803000	H	-12.828013000	15.353845000	18.049414000
H	-11.142286000	8.808787000	11.702790000	H	-14.541251000	14.898202000	17.828858000
H	-11.230065000	10.920277000	10.314752000	C	-9.742793000	8.064752000	16.724225000
H	-11.422138000	13.162223000	11.433600000	C	-8.606186000	9.053493000	16.373927000
N	-11.236063000	8.796784000	14.407499000	H	-8.750528000	10.031454000	16.876373000
P	-11.351178000	8.952210000	16.148239000	H	-7.633080000	8.623989000	16.699152000
H	-11.175964000	7.890526000	13.937048000	H	-8.547892000	9.240243000	15.281879000
H	-12.366100000	11.336126000	17.615902000	C	-9.791438000	7.860962000	18.252089000
H	-10.794881000	11.421385000	17.717191000	H	-10.508499000	7.069337000	18.550581000

H	-8.788013000	7.547477000	18.614402000
H	-10.061387000	8.797810000	18.782646000
C	-9.471002000	6.726327000	16.008021000
H	-8.478418000	6.339256000	16.327505000
H	-10.217853000	5.944709000	16.244124000
H	-9.422418000	6.849790000	14.906090000
C	-10.088323000	14.568580000	16.245462000
C	-8.882617000	13.747567000	15.729812000
H	-7.938878000	14.270944000	15.999702000
H	-8.862403000	12.733001000	16.180742000
H	-8.912677000	13.636247000	14.627072000
C	-10.080778000	15.948517000	15.559504000
H	-9.077921000	16.414754000	15.682305000
H	-10.288518000	15.854420000	14.474649000
H	-10.820678000	16.644219000	16.002283000
C	-9.988066000	14.709296000	17.776731000
H	-10.783315000	15.357447000	18.195816000
H	-10.043585000	13.722398000	18.280905000
H	-9.012555000	15.173957000	18.041643000
C	-12.942893000	7.952864000	16.570790000
C	-14.056460000	8.603297000	15.717292000
H	-13.894668000	8.446962000	14.631753000
H	-15.035431000	8.151149000	15.988182000
H	-14.113264000	9.696945000	15.898911000
C	-13.274218000	8.164459000	18.064402000
H	-13.319100000	9.243643000	18.315328000
H	-14.268310000	7.717874000	18.285499000
H	-12.539039000	7.682971000	18.738722000
C	-12.862318000	6.448662000	16.249110000
H	-12.166056000	5.906959000	16.920134000
H	-13.866972000	5.990626000	16.384797000
H	-12.560851000	6.253016000	15.198361000

NaO^tBu

$E_e^s = -395.2970373$

O	-11.282453000	9.114072000	8.535782000
C	-11.230418000	8.168725000	9.542693000
C	-11.172959000	8.866093000	10.931051000
H	-12.069966000	9.508587000	11.063239000
H	-10.276756000	9.521162000	10.982588000
H	-11.129737000	8.148985000	11.781012000
Na	-11.348441000	10.462516000	7.110295000
C	-9.966545000	7.278549000	9.377834000
H	-9.873826000	6.497039000	10.164764000
H	-9.992224000	6.774351000	8.387878000
H	-9.055664000	7.914364000	9.410256000
C	-12.491456000	7.260729000	9.491753000
H	-12.548227000	6.755992000	8.503361000
H	-12.501330000	6.478644000	10.283469000
H	-13.404459000	7.883775000	9.606504000

^tBuOH

$E_e^s = -233.5976047$

C	-11.283617000	8.163095000	9.609134000
C	-11.227990000	8.862877000	10.981976000
H	-12.143316000	9.469085000	11.140001000
H	-10.350815000	9.544021000	11.041617000

H	-11.140333000	8.134241000	11.815290000
C	-9.990867000	7.363694000	9.349990000
H	-9.842236000	6.561144000	10.102816000
H	-10.022704000	6.899456000	8.343114000
H	-9.100997000	8.029465000	9.392778000
C	-12.516095000	7.252755000	9.510709000
H	-12.567600000	6.786620000	8.505665000
H	-12.482539000	6.448528000	10.273334000
H	-13.442083000	7.844550000	9.660134000
O	-11.461998000	9.145488000	8.571492000
H	-10.688915000	9.740794000	8.610377000

IN1

$E_e^s = -1938.276833$

C	-11.008396000	11.024671000	11.302140000
Ir	-11.715905000	11.172060000	16.146885000
P	-11.755574000	13.449869000	15.647117000
N	-11.477031000	13.501017000	13.955868000
C	-11.330390000	12.326805000	13.353055000
N	-11.372224000	11.101945000	14.075028000
C	-11.220633000	9.858783000	13.460510000
C	-11.048629000	9.808076000	12.036652000
C	-11.114683000	12.254210000	11.926523000
H	-11.221573000	8.850538000	11.512790000
H	-10.906602000	10.981369000	10.203941000
H	-11.076974000	13.200852000	11.371400000
N	-11.162753000	8.707174000	14.195343000
P	-11.535450000	8.874969000	15.868379000
C	-13.456738000	14.332117000	15.803855000
C	-13.522161000	15.640968000	14.992146000
H	-12.945897000	16.461506000	15.461904000
H	-13.136436000	15.485794000	13.964602000
H	-14.580354000	15.978826000	14.923234000
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H	-14.439664000	12.355191000	15.736903000
H	-15.489422000	13.744033000	15.258855000
C	-13.813416000	14.576204000	17.282562000
H	-13.695516000	13.654601000	17.890142000
H	-13.194350000	15.375714000	17.738020000
H	-14.874832000	14.901185000	17.360182000
C	-10.039265000	8.017083000	16.741149000
C	-8.816550000	8.894350000	16.387479000
H	-9.002878000	9.959726000	16.638261000
H	-7.919170000	8.540272000	16.941134000
H	-8.569781000	8.861671000	15.302723000
C	-10.229916000	8.065003000	18.272062000
H	-11.040213000	7.392527000	18.615069000
H	-9.294164000	7.740682000	18.779231000
H	-10.467911000	9.093473000	18.612344000
C	-9.778137000	6.568659000	16.285733000
H	-8.784211000	6.225880000	16.651745000
H	-10.533160000	5.860189000	16.678333000
H	-9.786917000	6.467734000	15.177774000
C	-10.299476000	14.494010000	16.342325000
C	-9.033404000	13.722221000	15.901906000
H	-8.130573000	14.232324000	16.305478000
H	-9.049055000	12.678794000	16.281990000
H	-8.950124000	13.687361000	14.796758000
C	-10.248170000	15.915052000	15.749655000

H	-9.273042000	16.387735000	16.004276000
H	-10.341719000	15.890422000	14.645115000
H	-11.043736000	16.570051000	16.157690000
C	-10.351854000	14.537839000	17.882281000
H	-11.205966000	15.133647000	18.260966000
H	-10.425876000	13.518010000	18.313057000
H	-9.422338000	15.009718000	18.271813000
C	-13.158595000	7.847672000	16.041721000
C	-14.189002000	8.659979000	15.221434000
H	-13.900000000	8.720275000	14.152447000
H	-15.182637000	8.163365000	15.283010000
H	-14.286296000	9.695476000	15.609223000
C	-13.617824000	7.792693000	17.511575000
H	-13.610696000	8.800531000	17.976363000
H	-14.658147000	7.401488000	17.562228000
H	-12.988094000	7.119490000	18.127921000
C	-13.054265000	6.433417000	15.440506000
H	-12.450332000	5.746240000	16.065935000
H	-14.071013000	5.988370000	15.359008000
H	-12.615481000	6.467338000	14.422184000
H	-11.120126000	11.278963000	17.610551000
Na	-9.354192000	8.117212000	12.993139000
H	-12.675611000	11.202609000	17.415784000

3,3-dimethylbut-1-ene

$E_e^s = -235.7313971$

C	-0.040672000	1.484276000	-2.013277000
C	1.134501000	0.624460000	-2.516429000
H	2.092892000	0.927968000	-2.045392000
H	0.973457000	-0.452616000	-2.300967000
H	1.251389000	0.733142000	-3.615109000
C	0.224635000	2.974210000	-2.351662000
H	1.159142000	3.333117000	-1.872252000
H	0.322946000	3.116895000	-3.449221000
H	-0.606348000	3.622502000	-2.000792000
C	-1.349651000	1.032732000	-2.711555000
H	-1.269529000	1.153185000	-3.813254000
H	-1.570445000	-0.033557000	-2.496521000
H	-2.218532000	1.634138000	-2.369114000
C	-0.242665000	1.369024000	-0.508007000
H	-1.082688000	0.978680000	-0.119761000
C	0.464906000	0.632445000	0.368102000
H	1.313991000	0.000338000	0.060791000
H	0.216809000	0.634835000	1.441933000

IN2

$E_e^s = -2174.009880$

C	-11.807772000	10.658138000	11.110912000
Ir	-11.341886000	11.285144000	15.946706000
P	-11.523416000	13.504959000	15.249911000
N	-11.649361000	13.386935000	13.543979000
C	-11.640776000	12.157811000	13.041663000
N	-11.497088000	11.010053000	13.869477000
C	-11.479340000	9.711504000	13.360328000
C	-11.655948000	9.519833000	11.948855000
C	-11.772653000	11.943950000	11.619161000
H	-11.941369000	8.518402000	11.578658000
H	-11.973512000	10.506601000	10.030247000

H	-11.878830000	12.831598000	10.981594000
N	-11.228797000	8.637422000	14.167591000
P	-11.186537000	8.969651000	15.857211000
C	-13.151533000	14.419103000	15.710286000
C	-13.432799000	15.624660000	14.791460000
H	-12.771978000	16.486580000	15.006933000
H	-13.306353000	15.344900000	13.726399000
H	-14.480926000	15.966356000	14.944279000
C	-14.254688000	13.358123000	15.482868000
H	-14.288889000	13.033066000	14.422744000
H	-14.088220000	12.459784000	16.113560000
H	-15.245504000	13.794324000	15.740070000
C	-13.146088000	14.835860000	17.191933000
H	-12.869139000	13.996521000	17.858587000
H	-12.451016000	15.681494000	17.386971000
H	-14.163381000	15.182397000	17.484725000
C	-9.502004000	8.208712000	16.423118000
C	-8.422488000	9.001919000	15.652275000
H	-8.563493000	10.095983000	15.779095000
H	-7.409557000	8.720891000	16.015611000
H	-8.446161000	8.800112000	14.558151000
C	-9.293562000	8.472807000	17.929934000
H	-9.993681000	7.891346000	18.560253000
H	-8.260907000	8.180825000	18.224090000
H	-9.430294000	9.547282000	18.167172000
C	-9.348944000	6.705973000	16.122317000
H	-8.291752000	6.391407000	16.273664000
H	-9.974319000	6.078230000	16.787114000
H	-9.632555000	6.454576000	15.076317000
C	-9.958788000	14.595850000	15.481828000
C	-8.821472000	13.778476000	14.825618000
H	-7.856578000	14.317125000	14.956062000
H	-8.731029000	12.774493000	15.291629000
H	-9.001328000	13.641665000	13.740116000
C	-10.071233000	15.956560000	15.768351000
H	-9.071615000	16.445716000	14.743558000
H	-10.420198000	15.831765000	13.723364000
H	-10.759976000	16.649951000	15.291324000
C	-9.645247000	14.781090000	16.979828000
H	-10.395750000	15.411709000	17.496337000
H	-9.596142000	13.805343000	17.505549000
H	-8.658488000	15.283103000	17.092616000
C	-12.687297000	7.950168000	16.514022000
C	-13.913516000	8.728571000	15.980090000
H	-13.924538000	8.757633000	14.871243000
H	-14.846232000	8.225998000	16.319766000
H	-13.919347000	9.775008000	16.349748000
C	-12.723336000	7.944947000	18.053888000
H	-12.595919000	8.965077000	18.471950000
H	-13.707051000	7.558457000	18.401445000
H	-11.945171000	7.287562000	18.492829000
C	-12.736059000	6.514894000	15.955801000
H	-11.967197000	5.854358000	16.403096000
H	-13.726656000	6.062139000	16.184207000
H	-12.605877000	6.516326000	14.854339000
H	-10.389764000	11.534324000	17.184626000
Na	-9.773404000	7.895990000	12.621080000
H	-11.948136000	11.446794000	17.411195000
C	-12.828387000	12.006358000	23.170344000
C	-14.316049000	11.788985000	23.506933000
C	-12.392296000	13.418562000	23.639713000
C	-11.970601000	10.943201000	23.904196000

C	-12.547645000	11.895136000	21.677269000
H	-14.960839000	12.541698000	23.006960000
H	-14.661639000	10.781481000	23.193957000
H	-14.483014000	11.876971000	24.601120000
H	-12.990080000	14.208280000	23.138813000
H	-12.526212000	13.527845000	24.737501000
H	-11.322210000	13.607846000	23.409622000
H	-12.098865000	11.024508000	25.005083000
H	-12.259519000	9.916043000	23.598256000
H	-10.890204000	11.071592000	23.680120000
C	-11.484032000	12.046710000	21.406032000
H	-13.422865000	11.643487000	20.685868000
H	-14.497590000	11.482998000	20.871698000
H	-13.088772000	11.590942000	19.636333000

TS1

$E_e^S = -2173.988552$

C	-1.261016000	-3.542041000	-2.662089000
Ir	0.185133000	0.191763000	0.246827000
P	2.126719000	-1.180194000	0.221464000
N	1.704936000	-2.441136000	-0.828107000
C	0.471126000	-2.433214000	-1.327318000
N	-0.448428000	-1.417836000	-1.003633000
C	-1.785752000	-1.546040000	-1.317667000
C	-2.212667000	-2.595695000	-2.207283000
C	0.046199000	-3.492829000	-2.210235000
H	-3.197522000	-2.495634000	-2.696899000
H	-1.569091000	-4.322895000	-3.378210000
H	0.799463000	-4.240114000	-2.492980000
N	-2.734502000	-0.750427000	-0.733674000
P	-2.164412000	0.569102000	0.181414000
C	3.815325000	-0.659120000	-0.572450000
C	4.682742000	-1.872786000	-0.978877000
H	5.211746000	-2.334901000	-0.125736000
H	4.060211000	-2.644839000	-1.473267000
H	5.459492000	-1.531628000	-1.699337000
C	3.410606000	0.048422000	-1.884658000
H	2.937431000	-0.673028000	-2.581751000
H	2.685775000	0.866710000	-1.718019000
H	4.313213000	0.468814000	-2.380826000
C	4.603764000	0.275515000	0.362907000
H	3.983480000	1.105968000	0.752643000
H	5.020321000	-0.273711000	1.232112000
H	5.464677000	0.725701000	-0.180109000
C	-3.045138000	0.392331000	1.918333000
C	-2.834377000	-1.055742000	2.410341000
H	-1.796081000	-1.407910000	2.242309000
H	-3.051714000	-1.119388000	3.498922000
H	-3.539954000	-1.767619000	1.923674000
C	-2.334414000	1.344091000	2.905373000
H	-2.415346000	2.405022000	2.593400000
H	-2.795727000	1.258968000	3.914698000
H	-1.257952000	1.094049000	2.986517000
C	-4.560195000	0.673440000	1.924493000
H	-4.977186000	0.424813000	2.926695000
H	-4.798527000	1.737654000	1.731946000
H	-5.106246000	0.061453000	1.175576000
C	2.462007000	-2.066545000	1.922302000
C	1.259508000	-3.000408000	2.177053000
H	1.393337000	-3.512308000	3.155686000

H	0.304318000	-2.438571000	2.212473000
H	1.179123000	-3.769654000	1.382595000
C	3.728656000	-2.944707000	1.918790000
H	3.774054000	-3.517433000	2.872347000
H	3.716398000	-3.677109000	1.087258000
H	4.661048000	-2.349892000	1.855903000
C	2.549999000	-1.010373000	3.042469000
H	3.426370000	-0.341451000	2.920216000
H	1.640863000	-0.376362000	3.067751000
H	2.655523000	-1.516516000	4.028403000
C	-3.025199000	2.035495000	-0.787295000
C	-2.237755000	2.126117000	-2.114156000
H	-2.321745000	1.179509000	-2.686028000
H	-2.659895000	2.942835000	-2.740493000
H	-1.161340000	2.326461000	-1.964786000
C	-2.972280000	3.374019000	-0.025107000
H	-1.947460000	3.653973000	0.293074000
H	-3.348369000	4.192655000	-0.678889000
H	-3.612153000	3.365696000	0.881021000
C	-4.488238000	1.710775000	-1.164812000
H	-5.191746000	1.808182000	-0.317475000
H	-4.824065000	2.425197000	-1.949237000
H	-4.562966000	0.685560000	-1.579569000
H	-0.165907000	-0.742866000	1.493873000
Na	-3.815389000	-2.681946000	-0.255237000
H	0.744790000	1.464134000	-0.928017000
C	1.691744000	3.634150000	-0.765590000
C	3.193863000	3.461702000	-0.481208000
C	1.257651000	5.015064000	-0.202868000
C	1.443858000	3.615078000	-2.287450000
C	0.763441000	2.604294000	-0.034184000
H	3.408588000	3.472956000	0.607069000
H	3.592245000	2.522394000	-0.903425000
H	3.761008000	4.299472000	-0.939808000
H	1.395737000	5.060024000	0.897651000
H	1.866451000	5.825286000	-0.657345000
H	0.190694000	5.231348000	-0.423024000
H	2.048733000	4.396211000	-2.794724000
H	1.715577000	2.634437000	-2.730609000
H	0.377831000	3.809289000	-2.528139000
H	-0.267653000	2.964461000	-0.183342000
C	0.976067000	2.148065000	1.345588000
H	2.010656000	2.058746000	1.714942000
H	0.252536000	2.482205000	2.104860000

IN3

$E_e^S = -2174.032563$

C	-11.547356000	10.585547000	10.962756000
Ir	-11.493943000	11.336754000	15.865622000
P	-11.629743000	13.526584000	15.040459000
N	-11.545914000	13.358273000	13.352288000
C	-11.505110000	12.113145000	12.876599000
N	-11.446002000	10.999020000	13.737830000
C	-11.401422000	9.704448000	13.256880000
C	-11.486855000	9.470926000	11.838668000
C	-11.518276000	11.880203000	11.452674000
H	-11.773235000	8.465002000	11.480505000
H	-11.637755000	10.413646000	9.876384000
H	-11.553499000	12.759575000	10.795876000
N	-11.203615000	8.648035000	14.102981000

P	-11.241080000	8.989916000	15.784947000
C	-13.350585000	14.383429000	15.266577000
C	-13.647907000	15.387742000	14.134427000
H	-13.041812000	16.310363000	14.218565000
H	-13.447247000	14.936125000	13.143070000
H	-14.718750000	15.688014000	14.183911000
C	-14.354851000	13.210896000	15.158227000
H	-14.257186000	12.681034000	14.187737000
H	-14.214932000	12.474447000	15.978708000
H	-15.396237000	13.596913000	15.227717000
C	-13.501161000	15.063737000	16.640085000
H	-13.272293000	14.374177000	17.478220000
H	-12.853096000	15.958589000	16.737114000
H	-14.551885000	15.408233000	16.768523000
C	-9.596884000	8.127221000	16.363405000
C	-8.458049000	8.916156000	15.679399000
H	-8.494396000	9.992285000	15.943350000
H	-7.471211000	8.509213000	15.991310000
H	-8.507782000	8.869083000	14.569741000
C	-9.387860000	8.235813000	17.885649000
H	-10.162255000	7.689954000	18.458933000
H	-8.402698000	7.796141000	18.159237000
H	-9.394756000	9.290036000	18.221191000
C	-9.519843000	6.645030000	15.944651000
H	-8.479355000	6.267526000	16.065714000
H	-10.173279000	6.002998000	16.567507000
H	-9.828521000	6.485181000	14.888793000
C	-10.177363000	14.723038000	15.426454000
C	-8.924754000	14.049686000	14.821753000
H	-8.031731000	14.679573000	15.029810000
H	-8.748692000	13.046785000	15.263296000
H	-9.025863000	13.929801000	13.724602000
C	-10.371147000	16.095909000	14.753320000
H	-9.435985000	16.691633000	14.851658000
H	-10.594260000	15.983399000	13.673110000
H	-11.183841000	16.685131000	15.224332000
C	-9.986425000	14.876512000	16.948020000
H	-10.846026000	15.374245000	17.438582000
H	-9.838109000	13.893215000	17.438353000
H	-9.086013000	15.499121000	17.147840000
C	-12.803660000	7.991590000	16.347849000
C	-13.967210000	8.855855000	15.803804000
H	-13.915460000	8.963643000	14.700791000
H	-14.940292000	8.378594000	16.055223000
H	-13.967364000	9.871341000	16.255705000
C	-12.907664000	7.906834000	17.880854000
H	-12.768021000	8.897272000	18.360598000
H	-13.915744000	7.533339000	18.168416000
H	-12.167177000	7.203476000	18.313802000
C	-12.899573000	6.590894000	15.715351000
H	-12.184166000	5.872916000	16.162993000
H	-13.920003000	6.177479000	15.878969000
H	-12.716260000	6.639549000	14.622807000
H	-10.012540000	11.550035000	16.252201000
Na	-9.673454000	7.870742000	12.632819000
H	-11.074856000	10.159029000	19.071623000
C	-11.439862000	11.731641000	20.522005000
C	-12.886981000	11.325363000	20.875819000
C	-11.284021000	13.260510000	20.674968000
C	-10.471657000	11.036370000	21.505575000
C	-11.069293000	11.271647000	19.071536000
H	-13.626398000	11.827697000	20.218139000

H	-13.033647000	10.228317000	20.771520000
H	-13.132672000	11.597553000	21.925225000
H	-11.976693000	13.813983000	20.007815000
H	-11.498529000	13.580832000	21.717581000
H	-10.249705000	13.584657000	20.429644000
H	-10.678153000	11.332141000	22.557177000
H	-10.560315000	9.930115000	21.443490000
H	-9.415084000	11.300792000	21.283424000
H	-10.005851000	11.562470000	18.900445000
C	-11.933271000	11.783923000	17.908350000
H	-12.975980000	11.392038000	18.041733000
H	-12.024312000	12.885255000	18.023655000

TS2

$E_e^s = -2174.0215284$

C	-12.015996000	10.506039000	10.881918000
Ir	-11.574717000	11.286784000	15.697447000
P	-11.735089000	13.486721000	14.911413000
N	-11.831487000	13.307367000	13.222779000
C	-11.840273000	12.055999000	12.774276000
N	-11.717468000	10.947417000	13.651314000
C	-11.678659000	9.644026000	13.166125000
C	-11.862308000	9.403337000	11.759863000
C	-11.971494000	11.802942000	11.359884000
H	-12.142652000	8.384888000	11.435979000
H	-12.186323000	10.322583000	9.807138000
H	-12.067768000	12.678014000	10.703805000
N	-11.390968000	8.594356000	13.987753000
P	-11.331610000	8.964337000	15.661475000
C	-13.350847000	14.497050000	15.267361000
C	-13.622115000	15.545321000	14.167832000
H	-12.939470000	16.414353000	14.231690000
H	-13.513909000	15.094814000	13.161627000
H	-14.660587000	15.930429000	14.279370000
C	-14.476481000	13.437589000	15.216491000
H	-14.510984000	12.937307000	14.226761000
H	-14.339022000	12.650564000	15.986117000
H	-15.460173000	13.930266000	15.384458000
C	-13.340081000	15.173701000	16.650786000
H	-13.136220000	14.456435000	17.472329000
H	-12.596003000	15.993974000	16.712467000
H	-14.338101000	15.624672000	16.849799000
C	-9.601460000	8.236612000	16.163833000
C	-8.573615000	9.080455000	15.376205000
H	-8.762484000	10.166580000	15.514877000
H	-7.541009000	8.838710000	15.711990000
H	-8.613773000	8.891722000	14.280552000
C	-9.326599000	8.456524000	17.664195000
H	-10.026339000	7.892030000	18.311170000
H	-8.297012000	8.114538000	17.912670000
H	-9.399426000	9.528847000	17.930778000
C	-9.422005000	6.746148000	15.818238000
H	-8.347740000	6.462637000	15.893304000
H	-9.981781000	6.084595000	16.508538000
H	-9.770534000	6.506624000	14.789666000
C	-10.159962000	14.570986000	15.141906000
C	-9.029269000	13.761464000	14.467505000
H	-8.058654000	14.285858000	14.614179000
H	-8.955700000	12.744089000	14.907290000
H	-9.210269000	13.653183000	13.379263000

C	-10.276807000	15.941700000	14.448944000
H	-9.280534000	16.438636000	14.439849000
H	-10.613895000	15.830978000	13.398537000
H	-10.975363000	16.623415000	14.975476000
C	-9.827239000	14.741401000	16.637770000
H	-10.605059000	15.304875000	17.190731000
H	-9.692171000	13.758504000	17.134119000
H	-8.873799000	15.305597000	16.743972000
C	-12.782563000	7.858539000	16.325204000
C	-14.045840000	8.590581000	15.813000000
H	-14.066986000	8.630413000	14.704803000
H	-14.954783000	8.047735000	16.155616000
H	-14.093069000	9.634721000	16.186482000
C	-12.816013000	7.801545000	17.861884000
H	-12.786979000	8.813655000	18.314320000
H	-13.758560000	7.314693000	18.198107000
H	-11.977820000	7.208994000	18.282906000
C	-12.772923000	6.434454000	15.736320000
H	-11.984248000	5.793874000	16.178048000
H	-13.748072000	5.940793000	15.946705000
H	-12.632654000	6.466136000	14.636940000
H	-10.762681000	11.599941000	17.069179000
Na	-9.910560000	7.905946000	12.429377000
H	-11.301215000	10.109843000	19.108617000
C	-11.941781000	11.636388000	20.525669000
C	-13.429381000	11.223978000	20.577922000
C	-11.820739000	13.160164000	20.749971000
C	-11.179110000	10.906174000	21.654455000
C	-11.290589000	11.219566000	19.168245000
H	-14.032058000	11.749801000	19.808433000
H	-13.551725000	10.131602000	20.415310000
H	-13.871318000	11.465973000	21.568204000
H	-12.387253000	13.738724000	19.991187000
H	-12.220319000	13.445146000	21.746722000
H	-10.760877000	13.490997000	20.705491000
H	-11.591244000	11.168261000	22.652438000
H	-11.248450000	9.803142000	21.539900000
H	-10.101436000	11.177182000	21.653515000
H	-10.213339000	11.504880000	19.219343000
C	-11.927532000	11.802477000	17.893709000
H	-12.966919000	11.428901000	17.772814000
H	-11.965211000	12.903736000	17.974487000

2,2-dimethylbutane
 $E_e^s = -236.9644481$

C	-0.032860000	-0.019772000	-0.511163000
C	-1.319085000	-0.663483000	-1.075513000
H	-1.351106000	-0.578520000	-2.182745000
H	-1.387180000	-1.743073000	-0.826462000
H	-2.228234000	-0.165600000	-0.674676000
C	0.017089000	1.462472000	-0.944964000
H	0.932515000	1.963452000	-0.563176000
H	0.017326000	1.558621000	-2.051789000
H	-0.859536000	2.025176000	-0.558157000
C	1.203469000	-0.750185000	-1.081396000
H	2.146471000	-0.317085000	-0.683554000
H	1.197548000	-1.832292000	-0.834078000
H	1.236993000	-0.665921000	-2.188633000
C	-0.030806000	-0.064373000	1.046007000
H	0.875536000	0.477137000	1.402022000

H	-0.896916000	0.536965000	1.406115000
C	-0.075960000	-1.448509000	1.707544000
H	0.798212000	-2.074408000	1.431013000
H	-0.991402000	-2.014244000	1.434923000
H	-0.070360000	-1.353232000	2.813445000

IN4
 $E_e^s = -1937.041566$

C	-10.371013000	11.169584000	11.381840000
Ir	-11.762345000	11.057992000	15.978430000
P	-11.837077000	13.350230000	15.651523000
N	-11.322016000	13.507744000	14.037720000
C	-11.053186000	12.358960000	13.422673000
N	-11.170041000	11.097218000	14.081732000
C	-10.871883000	9.894720000	13.434992000
C	-10.483221000	9.927074000	12.053413000
C	-10.619764000	12.355483000	12.049038000
H	-10.540793000	8.982058000	11.484374000
H	-10.100850000	11.186293000	13.312444000
H	-10.528106000	13.337320000	11.565530000
N	-10.868169000	8.699942000	14.103982000
P	-11.499695000	8.787381000	15.690165000
C	-13.563900000	14.197605000	15.629510000
C	-13.553598000	15.541646000	14.874120000
H	-13.065284000	16.351884000	15.449047000
H	-13.029681000	15.438309000	13.902380000
H	-14.600713000	15.862346000	14.674981000
C	-14.460885000	13.204673000	14.853435000
H	-14.106731000	13.076177000	13.810078000
H	-14.465532000	12.202708000	15.333070000
H	-15.502721000	13.594632000	14.818454000
C	-14.109804000	14.365820000	17.059921000
H	-14.069960000	13.412525000	17.630220000
H	-13.558490000	15.138138000	17.634720000
H	-15.175047000	14.685566000	17.020738000
C	-10.151546000	7.883608000	16.744358000
C	-8.941186000	8.845142000	16.744858000
H	-9.245045000	9.870990000	17.045880000
H	-8.151581000	8.470408000	17.433458000
H	-8.479732000	8.941855000	15.736118000
C	-10.645847000	7.729983000	18.197148000
H	-11.463998000	6.987110000	18.284512000
H	-9.814387000	7.383760000	18.850686000
H	-11.010921000	8.697317000	18.603479000
C	-9.709011000	6.516745000	16.186594000
H	-8.778056000	6.178358000	16.694780000
H	-10.470288000	5.727526000	16.332638000
H	-9.504187000	6.562739000	15.094067000
C	-10.545331000	14.359325000	16.659018000
C	-9.183061000	13.757153000	16.246497000
H	-8.373516000	14.215108000	16.857722000
H	-9.173241000	12.657431000	16.409003000
H	-8.968881000	13.948140000	15.175806000
C	-10.547759000	15.865538000	16.342682000
H	-9.658696000	16.346571000	16.809573000
H	-10.497226000	16.047467000	15.249892000
H	-11.444108000	16.379852000	16.744757000
C	-10.764678000	14.110083000	18.165842000
H	-11.718835000	14.535006000	18.536656000
H	-10.759749000	13.021777000	18.392507000

H	-9.942514000	14.581917000	18.749470000	13.564736000	
C	-13.134028000	7.761620000	15.623673000	C	-10.399223000 9.929720000
C	-13.922435000	8.399427000	14.456941000	12.187744000	
H	-13.413097000	8.234613000	13.486478000	C	-10.770515000 12.326972000
H	-14.936762000	7.945415000	14.404263000	12.106156000	
H	-14.032944000	9.495177000	14.603622000	H	-10.347696000 8.963217000
C	-13.925363000	7.976073000	16.930810000	11.656878000	
H	-14.057131000	9.059815000	17.138612000	H	-10.130381000 11.163162000
H	-14.937628000	7.523195000	16.836364000	10.405158000	
H	-13.438575000	7.511484000	17.811833000	H	-10.772557000 13.299435000
C	-12.936660000	6.262455000	15.339245000	11.596140000	
H	-12.510699000	5.717715000	16.206713000	N	-10.717952000 8.736550000
H	-13.919823000	5.791248000	15.114294000	14.259950000	
H	-12.280384000	6.099685000	14.459308000	P	-11.482215000 8.775860000
Na	-8.817058000	8.365903000	13.226854000	15.785438000	

Cyclooctane
 $E_e^s = -314.3326228$

C	-0.525544000	0.010444000	-4.514048000	15.808634000	14.242467000
C	0.458347000	0.846474000	-3.665932000	C	-13.668578000 15.466032000
C	-1.668470000	-0.481979000	-1.180250000	14.871660000	
C	1.201588000	0.049177000	-2.565130000	H	-13.100557000 16.333135000
C	-0.681602000	0.650298000	-0.817871000	15.260491000	
C	0.816011000	0.433264000	-1.119652000	H	-13.270490000 15.212774000
H	0.051921000	-0.560488000	-5.276652000	13.869102000	
H	-0.087786000	1.696218000	-3.201223000	H	-14.729454000 15.785796000
H	1.025924000	-1.038461000	-2.714963000	14.764488000	
H	-1.198167000	-1.473939000	-0.983049000	C	-14.595107000 13.177251000
H	-0.760612000	0.847182000	0.274084000	15.291706000	
H	-1.171425000	0.707239000	-5.095015000	H	-14.369453000 12.899654000
H	1.186906000	1.323230000	-4.356281000	14.241721000	
H	-2.518264000	-0.418163000	-0.465528000	H	-14.551332000 12.245945000
H	2.300411000	0.175037000	-2.672064000	15.895165000	
H	-1.033143000	1.591245000	-1.299359000	H	-15.630263000 13.585301000
H	1.214570000	-0.344373000	-0.429250000	15.325412000	
H	1.346845000	1.372720000	-0.842800000	C	-13.972984000 14.649755000
C	-1.422649000	-1.001388000	-3.770795000	17.245972000	
H	-0.808500000	-1.855657000	-3.404981000	H	-13.888078000 13.803528000
H	-2.097924000	-1.447591000	-4.533869000	17.959014000	
C	-2.287421000	-0.484586000	-2.599388000	H	-13.345837000 15.483751000
H	-2.673892000	0.535236000	-2.833142000	17.622392000	
H	-3.190997000	-1.131136000	-2.548396000	H	-15.029508000 14.998768000

IN5
 $E_e^s = -2251.401290$

C	-10.403626000	11.153666000	16.252777000	17.571575000	9.715935000
	11.473955000		C	-8.363026000	8.304247000
Ir	-11.781359000	11.056427000	17.893665000	17.893665000	
	16.145452000		H	-8.508756000	9.012205000
P	-11.883759000	13.358961000	16.252777000	16.252777000	
	15.727525000		C	-10.883335000	7.329003000
N	-11.521270000	13.469933000	18.198658000	18.198658000	
	14.072509000		H	-11.640666000	6.534081000
C	-11.183126000	12.325952000	18.045827000	18.045827000	
	13.487832000		H	-10.110475000	6.918653000
N	-11.194942000	11.091826000	18.886342000	18.886342000	
	14.192615000		H	-11.373566000	8.175514000
C	-10.805466000	9.910233000	18.719547000	18.719547000	
			C	-9.645180000	6.523141000
			16.167935000		
			H	-8.779538000	6.133419000

16.749470000	
H -10.377506000	5.699888000
16.071129000	
H -9.294414000	6.758186000
15.140465000	
C -10.483715000	14.453309000
16.492239000	
C -9.175904000	13.765023000
16.038297000	
H -8.304718000	14.280574000
16.501354000	
H -9.165062000	12.696524000
16.345971000	
H -9.063407000	13.808254000
14.936460000	
C -10.504734000	15.896356000
15.955900000	
H -9.561941000	16.414474000
16.243692000	
H -10.580181000	15.907264000
14.849858000	
H -11.342601000	16.489877000
16.375219000	
C -10.536388000	14.441431000
18.029908000	
H -11.459811000	14.903087000
18.433031000	
H -10.461984000	13.406331000
18.420765000	
H -9.675893000	15.016336000
18.440422000	
C -13.090943000	7.735689000
15.476876000	
C -13.793211000	8.474042000
14.314093000	
H -13.199451000	8.420716000
13.379944000	
H -14.783647000	8.004062000
14.123604000	
H -13.950889000	9.545927000
14.559921000	
C -14.018191000	7.769838000
16.705406000	
H -14.259121000	8.816397000
16.982504000	
H -14.976705000	7.257082000
16.466237000	
H -13.587350000	7.264640000
17.592871000	
C -12.802998000	6.285481000
15.049549000	
H -12.441604000	5.657799000
15.890335000	
H -13.739203000	5.813746000
14.674799000	
H -12.056618000	6.250538000
14.229517000	
C -14.135284000	10.984979000
19.000281000	
C -12.616864000	11.209265000
18.792214000	
C -13.307558000	12.569212000

22.073752000	
C -11.702827000	10.671007000
19.917287000	
C -12.010608000	12.909847000
21.310030000	
C -11.108939000	11.745422000
20.857446000	
H -14.394984000	9.981656000
18.600574000	
H -12.397190000	12.274487000
18.608148000	
H -12.263630000	9.914667000
20.508219000	
H -13.140350000	11.683350000
22.730688000	
H -11.381439000	13.559170000
21.957747000	
H -14.688871000	11.703815000
18.358519000	
H -12.370081000	10.562684000
17.849727000	
H -13.519183000	13.410719000
22.769457000	
H -10.850158000	10.119901000
19.472310000	
H -12.267604000	13.549224000
20.435693000	
H -10.706001000	11.229942000
21.758676000	
H -10.222758000	12.195099000
20.356699000	
C -14.705483000	11.039251000
20.434214000	
H -14.287534000	10.205804000
21.043670000	
H -15.786204000	10.796466000
20.332063000	
C -14.586364000	12.350920000
21.237379000	
H -14.734697000	13.222801000
20.558412000	
H -15.443785000	12.384484000
21.945267000	
Na -8.581530000	8.706555000
13.524951000	

TS3

$$E_e^s = -2251.3855613$$

C -11.625478000	10.972666000	11.216456000
Ir -12.031737000	11.144596000	16.092222000
P -11.955733000	13.427948000	15.577250000
N -11.761623000	13.462763000	13.887936000
C -11.731900000	12.276580000	13.291150000
N -11.790956000	11.067928000	14.032785000
C -11.650944000	9.836538000	13.404362000
C -11.620285000	9.769748000	11.966402000
C -11.635812000	12.199810000	11.853349000
H -11.863438000	8.806935000	11.481459000
H -11.629841000	10.924683000	10.113979000
H -11.608688000	13.151057000	11.305759000

H	-14.297198000	13.139922000	H	-10.167075000	13.526994000
14.282204000			18.240211000		
H	-14.510553000	12.594809000	H	-9.292795000	15.093715000
15.983128000			18.158214000		
H	-15.488941000	13.957222000	C	-13.135309000	7.764323000
15.348602000			16.108663000		
C	-13.688523000	14.997833000	C	-14.159296000	8.510077000
17.196798000			15.220507000		
H	-13.597034000	14.186183000	H	-13.801411000	8.607399000
17.946842000			14.176068000		
H	-13.001935000	15.817372000	H	-15.119313000	7.948211000
17.493240000			15.207402000		
H	-14.723842000	15.401364000	H	-14.377460000	9.528843000
17.261585000			15.606306000		
C	-10.040007000	7.949443000	C	-13.701463000	7.649063000
16.812842000			17.535908000		
C	-8.922551000	8.994727000	H	-13.809226000	8.639119000
17.024743000			18.018481000		
H	-9.205557000	9.752735000	H	-14.713225000	7.187118000
17.781332000			17.495053000		
H	-7.994891000	8.489481000	H	-13.080407000	7.012729000
17.375897000			18.194470000		
H	-8.685171000	9.538596000	C	-12.901458000	6.362394000
16.085297000			15.515687000		
C	-10.419393000	7.330324000	H	-12.260024000	5.730346000
18.174335000			16.164402000		
H	-11.063749000	6.435620000	H	-13.875430000	5.832900000
18.060556000			15.413282000		
H	-9.496929000	7.004707000	H	-12.443014000	6.429517000
18.704947000			14.507776000		
H	-10.941738000	8.054848000	C	-13.953964000	11.317475000
18.828551000			18.373459000		
C	-9.468326000	6.829571000	C	-12.404111000	11.500660000
15.909889000			18.352351000		
H	-8.783931000	6.188413000	C	-13.541660000	11.699305000
16.508402000			21.854978000		
H	-10.240933000	6.177219000	C	-11.656958000	10.668693000
15.461484000			19.426006000		
H	-8.833653000	7.246981000	C	-12.237202000	12.366814000
15.096534000			21.369984000		
C	-10.256460000	14.534515000	C	-11.205205000	11.457402000
16.283503000			20.677573000		
C	-9.005738000	13.806684000	H	-14.250718000	10.615526000
15.741324000			17.553498000		
H	-8.092292000	14.341494000	H	-12.202032000	12.563987000
16.083721000			18.605468000		
H	-8.948696000	12.761040000	H	-12.274033000	9.796620000
16.109088000			19.740438000		
H	-9.006752000	13.783019000	H	-13.334593000	10.650792000
14.633201000			22.174588000		
C	-10.262410000	15.970237000	H	-11.727844000	12.832373000
15.722726000			22.242799000		
H	-9.288107000	16.458021000	H	-14.435352000	12.279701000
15.950713000			18.094031000		
H	-10.397052000	15.970910000	H	-10.370083000	11.391191000
14.622412000			16.772028000		
H	-11.054175000	16.597551000	H	-13.875390000	12.223385000
16.179305000			22.777961000		
C	-10.206168000	14.553247000	H	-10.740093000	10.219513000
17.823117000			18.994521000		
H	-11.077514000	15.070338000	H	-12.497483000	13.217542000
18.271983000			20.700091000		

H	-10.803123000	10.737314000
	21.428338000	
H	-10.339173000	12.098099000
	20.391609000	
C	-14.686869000	10.798188000
	19.638148000	
H	-14.293370000	9.800662000
	19.939041000	
H	-15.737494000	10.604833000
	19.324728000	
C	-14.738071000	11.710758000
	20.881025000	
H	-14.931467000	12.760794000
	20.558012000	
H	-15.636588000	11.415728000
	21.468301000	
Na	-9.469361000	8.139177000
	13.019107000	

TS4

$E_e^s = -2251.3770291$

C	-11.762731000	10.888558000	11.573788000
Ir	-12.033214000	11.414617000	16.512185000
P	-11.869499000	13.666214000	15.762646000
N	-11.892690000	13.550405000	14.079019000
C	-11.874908000	12.324322000	13.555183000
N	-11.883361000	11.181570000	14.367258000
C	-11.677942000	9.929293000	13.840254000
C	-11.659452000	9.749307000	12.409094000
C	-11.832550000	12.157494000	12.122863000
H	-11.833953000	8.735915000	12.004496000
H	-11.791029000	10.759246000	10.478289000
H	-11.866234000	13.067645000	11.509515000
N	-11.412109000	8.859524000	14.644439000
P	-11.673571000	9.033323000	16.323902000
C	-13.305824000	14.951352000	16.026757000
C	-13.189677000	16.143187000	15.046562000
H	-12.436167000	16.888987000	15.356532000
H	-12.941355000	15.783645000	14.028173000
H	-14.170519000	16.666984000	15.004195000
C	-14.607044000	14.208409000	15.639917000
H	-14.572433000	13.899937000	14.575458000
H	-14.797362000	13.300431000	16.241292000
H	-15.471101000	14.896378000	15.771432000
C	-13.361898000	15.466018000	17.478714000
H	-13.427397000	14.650130000	18.227370000
H	-12.474012000	16.081373000	17.731939000
H	-14.256483000	16.114203000	17.614161000
C	-10.034912000	8.242987000	17.075928000
C	-9.006691000	9.364993000	17.325101000
H	-9.365977000	10.098184000	18.072304000
H	-8.057503000	8.917134000	17.697554000
H	-8.781311000	9.934563000	16.400099000
C	-10.316385000	7.537419000	18.419513000
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IN7

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Cyclooctene							
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C	-0.172110000	-0.414834000	0.608496000				
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H	-1.624956000	-0.602189000	-0.956683000				

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NMR Spectra

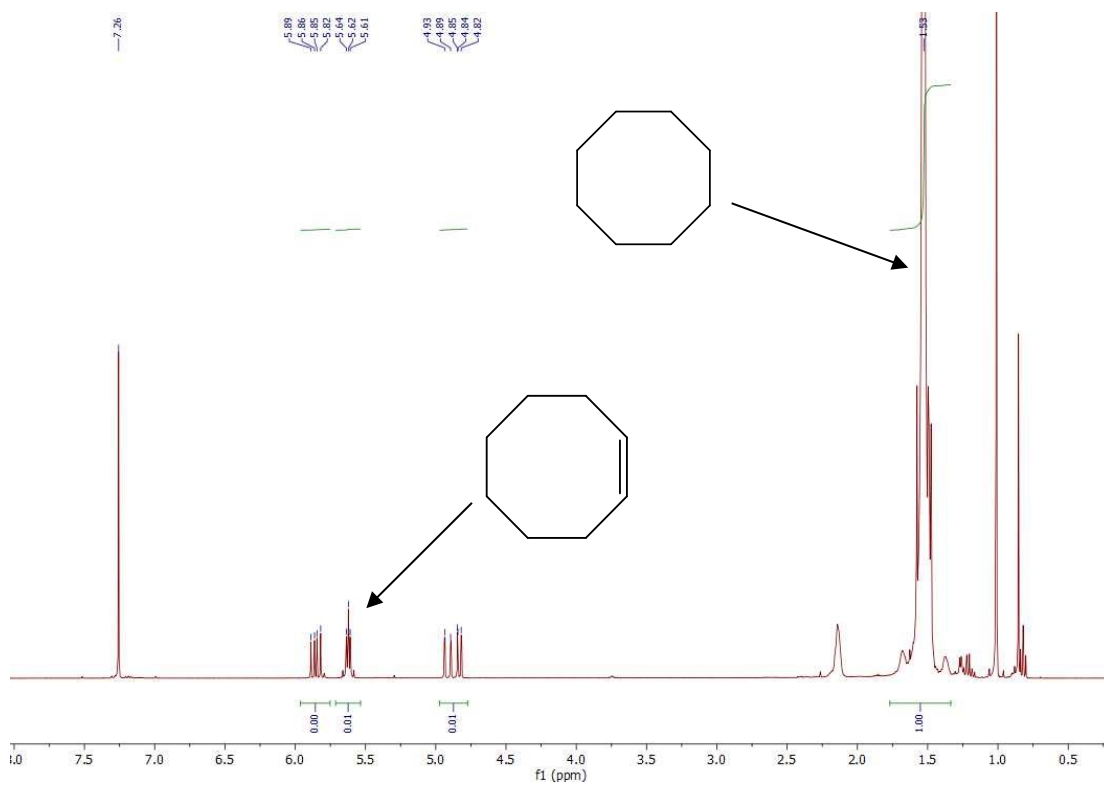


Figure 1: NMR spectra of COA (3.0 mmol), TBE (3.0 mmol), Ir2 (3.0 μ mol), and NaOtBu (15.0 μ mol).

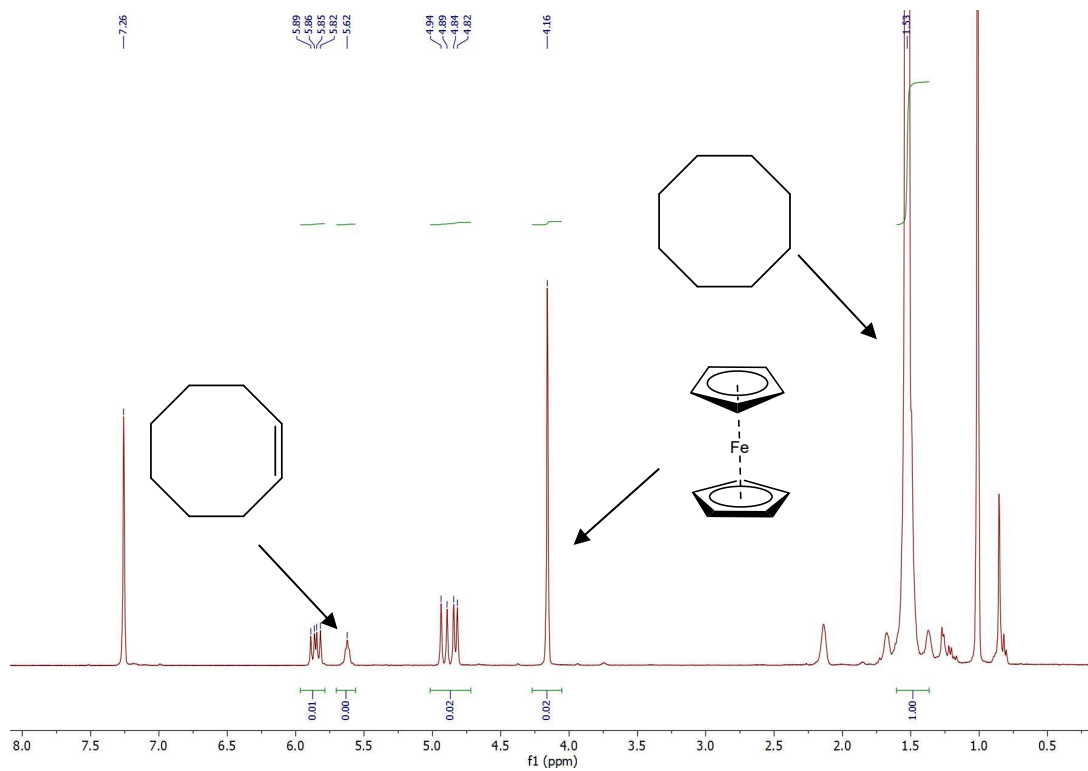


Figure 2: NMR spectra of COA (3.0 mmol), TBE (3.0 mmol), Ir2 (3.0 μ mol), NaOtBu (15.0 μ mol), and Fe (15.0 μ mol).

GC-MS Spectra

I. GC-MS spectra of reaction condition optimization for cyclooctane dehydrogenation

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.430	186	190	195	BB	67843	724525	0.07%	0.058%
2	1.616	209	216	225	BV	539082	6218071	0.57%	0.496%
3	1.750	225	236	242	VV	6026830	95143559	8.69%	7.585%
4	1.824	242	246	255	VV	963971	14512322	1.33%	1.157%
5	2.346	317	320	329	BV 3	59737	1733696	0.16%	0.138%
6	2.417	329	330	354	VV 5	31423	1394427	0.13%	0.111%
7	8.472	1171	1188	1212	BV	1152564	35824326	3.27%	2.856%
8	9.447	1283	1326	1350	BV	11326526	1094415859	100.00%	87.243%
9	12.170	1705	1712	1736	BV	56492	2057007	0.19%	0.164%
10	12.387	1736	1743	1755	PV 4	23636	684236	0.06%	0.055%
11	14.959	2098	2108	2138	BB 5	33474	1738489	0.16%	0.139%

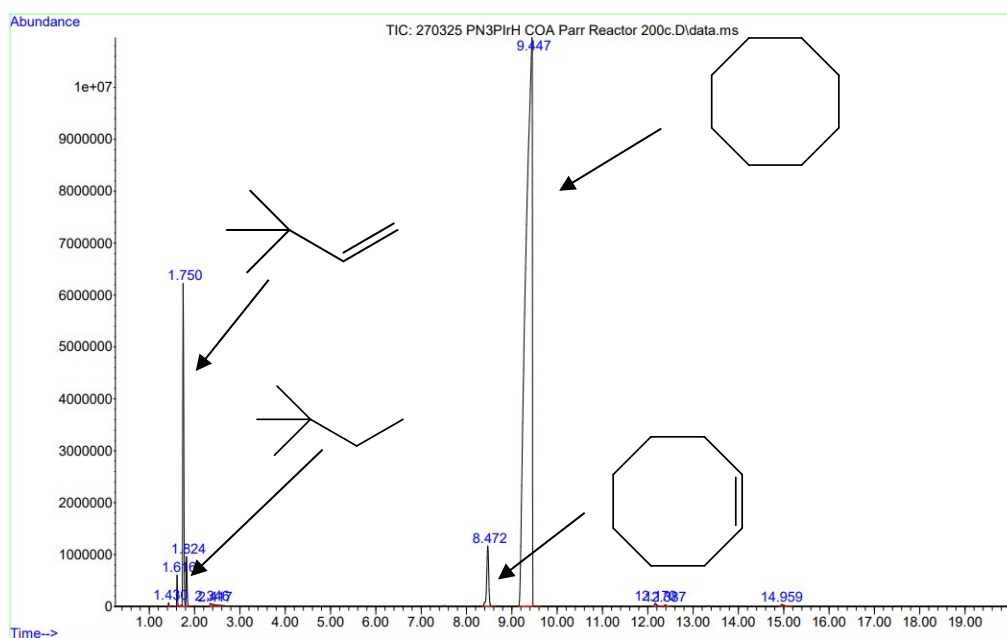


Figure 3: GC-MS spectra of COA (3.0 mmol), TBE (3.0 mmol), Ir2 (3.0 μ mol), NaO^tBu (15.0 μ mol).

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.430	184	190	196	BB	141497	1511597	0.16%	0.122%
2	1.507	197	201	210	BB 2	155685	2394808	0.25%	0.193%
3	1.615	211	216	224	BB	877998	9606598	0.99%	0.775%
4	1.749	224	235	242	BB	6270256	95211298	9.78%	7.681%
5	1.822	242	246	254	BB	1052024	15923575	1.64%	1.285%
6	8.449	1167	1185	1203	BB	1586277	43124646	4.43%	3.479%
7	9.359	1281	1314	1316	BB	12979010	973201372	100.00%	78.507%
8	20.071	2822	2832	2859	BB	4684067	98657763	10.14%	7.959%

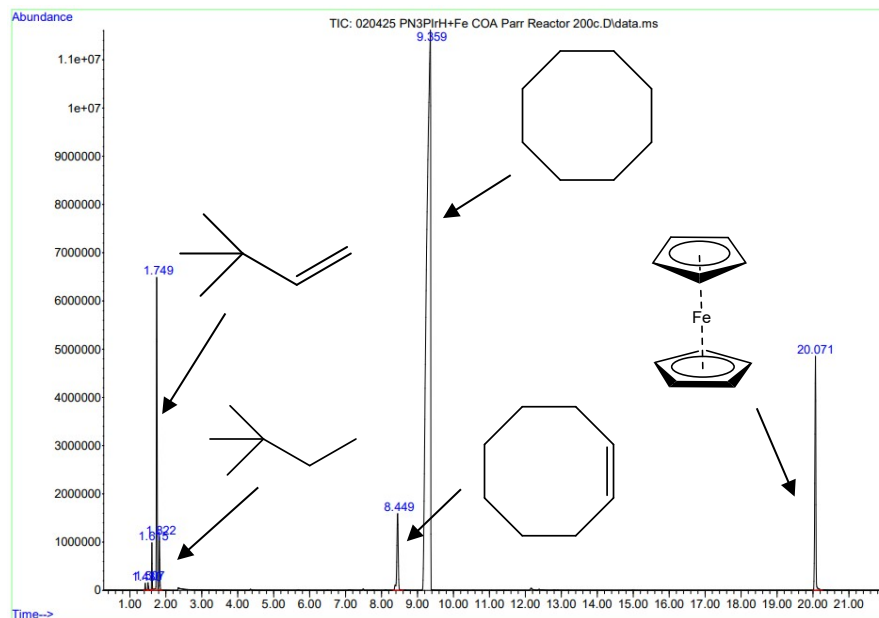


Figure 4: GC-MS spectra of COA (3.0 mmol), TBE (3.0 mmol), Ir2 (3.0 μ mol), NaO^tBu (15.0 μ mol), and Fe (15.0 μ mol).

II. GC-MS spectra of the effect of different ratios of tert-butylethylene (TBE) for cyclooctane dehydrogenation

GC-MS spectra were collected to evaluate the effect of varying TBE ratios on cyclooctane dehydrogenation. The resulting changes in product distribution are shown below for 0.3mmol, 1.5mmol and 3mmol of TBE, corresponding to a 1:1000:100, 1:1000:500, and 1:1000:1000 ratio of [Ir2]:COA:TBE respectively.

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.418	184	188	195	BB	259738	2700949	0.11%	0.098%
2	1.646	218	221	227	BB	1140465	17232893	0.73%	0.627%
3	1.714	227	230	238	BB	10772795	127622352	5.37%	4.647%
4	1.795	238	242	250	BB 2	723313	10561596	0.44%	0.385%
5	8.359	1155	1172	1194	BB 7	286296	17820227	0.75%	0.649%
6	9.383	1268	1317	1341	BB	19684188	2374626420	100.00%	86.459%
7	10.696	1491	1504	1546	BB	6650526	195966333	8.25%	7.135%

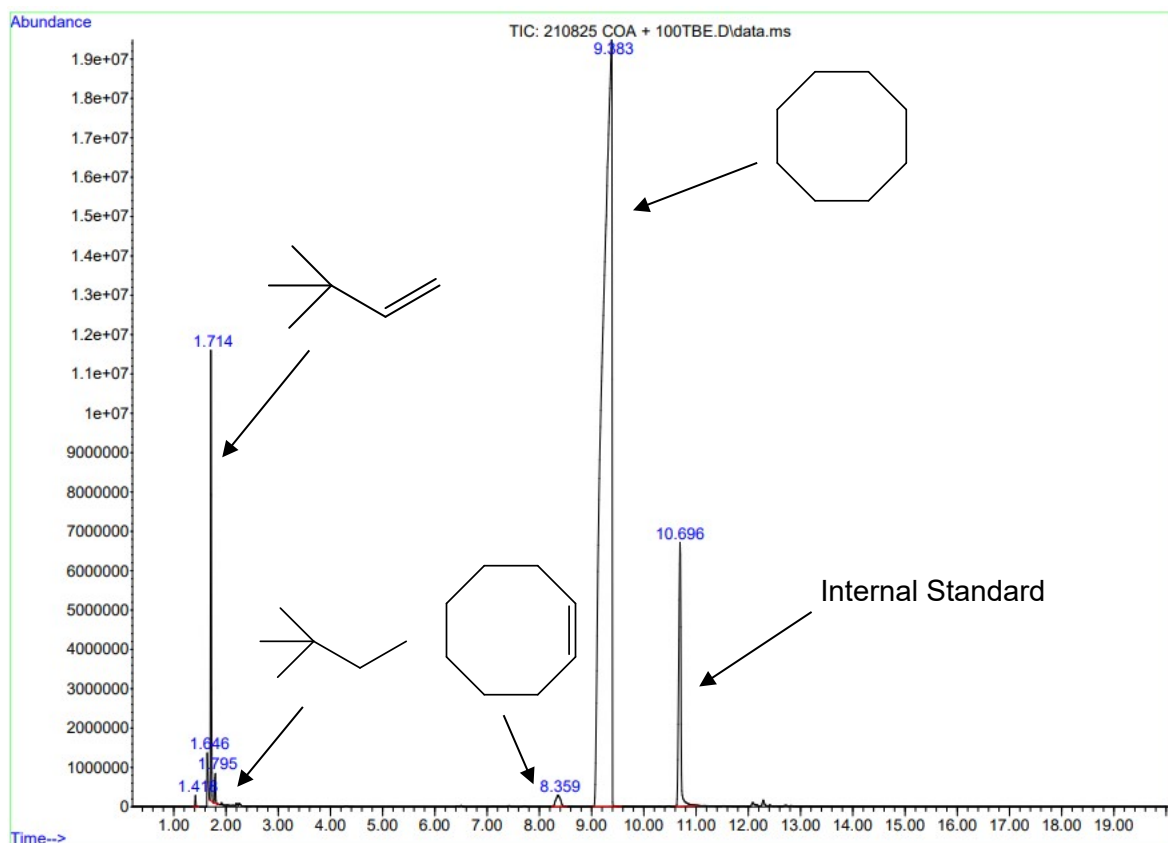


Figure 5: GC-MS spectra of COA (3.0 mmol), TBE (0.3mmol), Ir2 (3.0 μ mol), and NaO^tBu (15.0 μ mol).

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.417	182	188	195	BB	219316	2341654	0.14%	0.108%
2	1.646	218	221	227	BB	1240011	18036549	1.07%	0.830%
3	1.713	227	230	238	BB	19385606	256818244	15.23%	11.825%
4	1.792	238	241	249	BB 2	515919	7823214	0.46%	0.360%
5	1.917	256	259	269	BB	166369	1887853	0.11%	0.087%
6	8.361	1157	1172	1192	BB 6	159930	10172573	0.60%	0.468%
7	9.330	1264	1310	1316	BB	16701150	1686727523	100.00%	77.664%
8	10.690	1490	1503	1558	BB	6186046	188026891	11.15%	8.658%

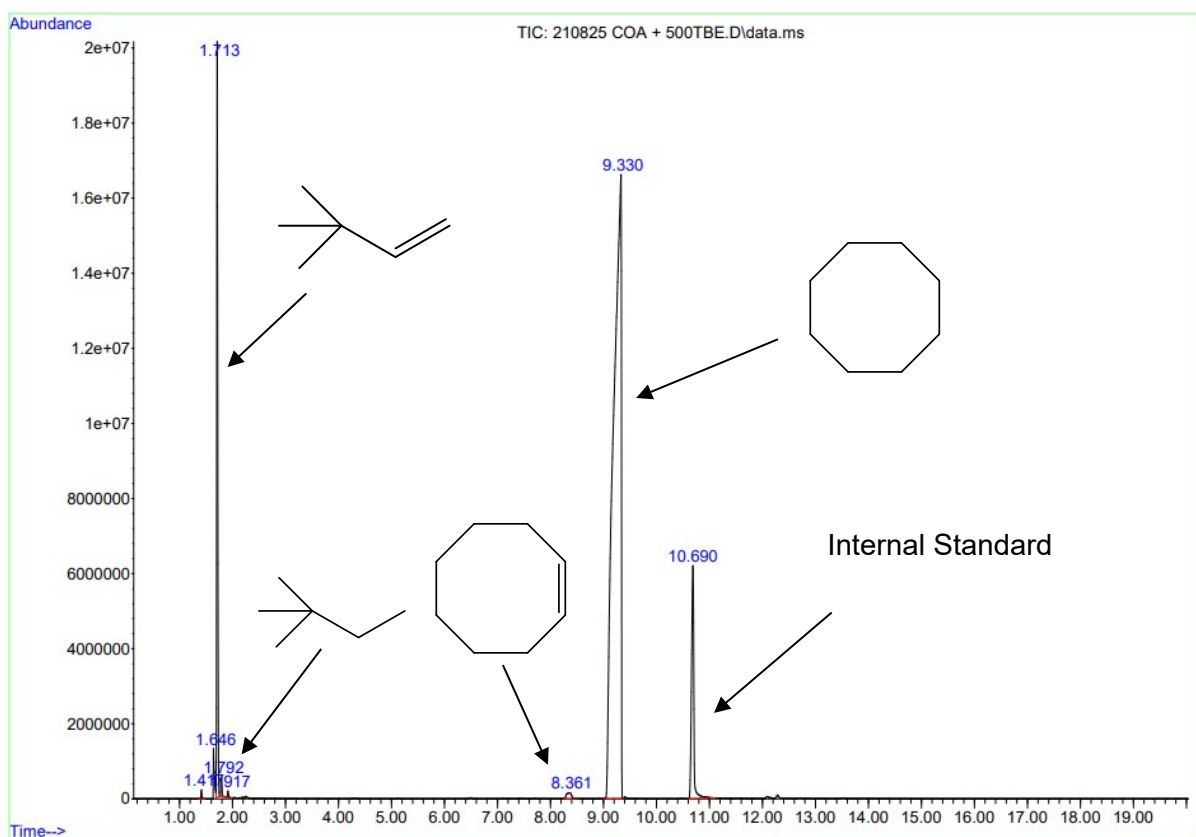


Figure 6: GC-MS spectra of COA (3.0 mmol), TBE (1.5 mmol), Ir2 (3.0 μ mol), and NaO^tBu (15.0 μ mol).

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.418	183	188	195	BB	225815	2356796	0.18%	0.130%
2	1.645	218	221	227	BB	1245597	18014753	1.40%	0.994%
3	1.712	227	230	238	BB	21135752	300896430	23.33%	16.610%
4	1.796	238	242	249	BB 2	420861	5888442	0.46%	0.325%
5	1.916	256	259	271	BBA	239707	2531675	0.20%	0.140%
6	8.364	1156	1173	1185	BB 5	123822	5292639	0.41%	0.292%
7	9.294	1265	1305	1311	BB	15097791	1289928539	100.00%	71.207%
8	10.690	1489	1503	1564	BB	6031873	186616372	14.47%	10.302%

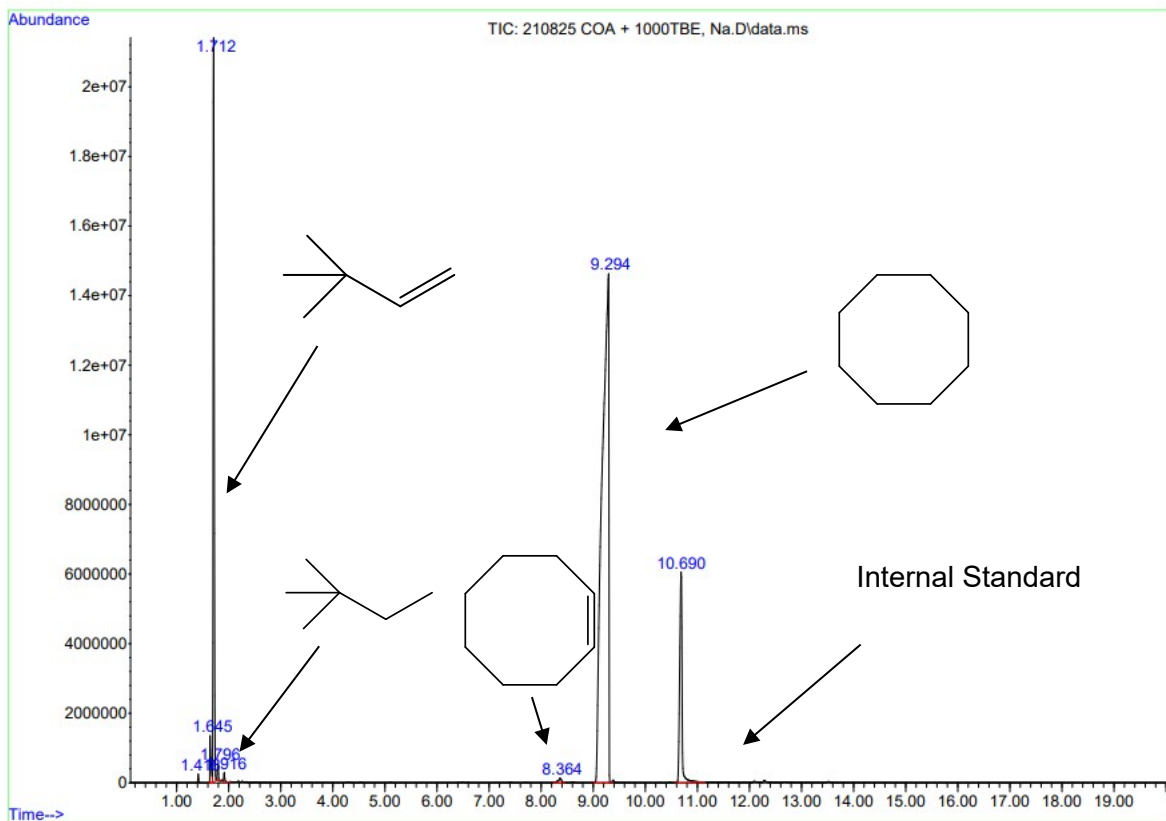


Figure 7: GC-MS spectra of COA (3.0 mmol), TBE (3.0 mmol), Ir2 (3.0 μ mol), and NaO^tBu (15.0 μ mol).

III. Time dependent study for cyclooctane dehydrogenation

GC-MS spectra were collected for cyclooctane dehydrogenation reactions run for 4 h, 16 h, and 24 h. The data shows an increase in the product formation over time up to 24h. GC-MS spectra were collected for the dehydrogenation of cyclooctane using KO^tBu and NaO^tBu. Only the KO^tBu data are shown here, as both bases exhibited similar trends in product formation over time.

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.418	184	188	195	BB	383339	3953817	0.26%	0.186%
2	1.646	218	221	226	BB	809127	10591548	0.70%	0.498%
3	1.711	226	230	238	BB	21891215	323718962	21.35%	15.216%
4	1.800	238	243	249	BB 2	295588	3766414	0.25%	0.177%
5	1.914	256	259	271	BBA	274209	2670903	0.18%	0.126%
6	8.361	1158	1173	1188	BB 2	67224	2451716	0.16%	0.115%
7	9.260	1264	1300	1308	BB	17201639	1516538993	100.00%	71.285%
8	9.362	1309	1314	1329	BB	165997	3532174	0.23%	0.166%
9	10.683	1488	1502	1536	BB	8500236	260200288	17.16%	12.231%

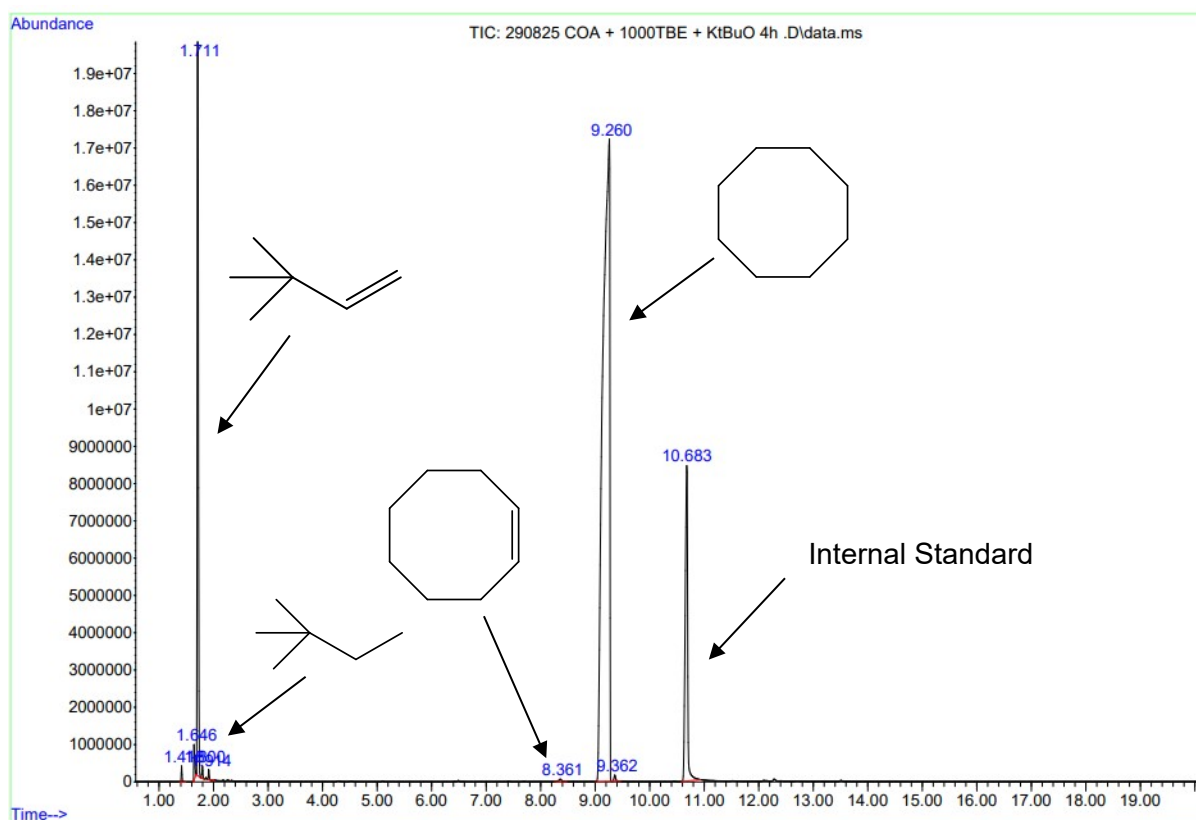


Figure 8: GC-MS spectra of COA (3.0 mmol), TBE (3.0 mmol), Ir2 (3.0 μmol), and KO^tBu (15.0 μmol) after 4h.

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.417	183	188	195	BB	406502	4232258	0.23%	0.171%
2	1.646	218	221	226	BB	793203	10158765	0.56%	0.409%
3	1.711	226	230	238	BB	22932270	360431452	20.01%	14.521%
4	1.797	238	242	249	BB 2	838493	11016482	0.61%	0.444%
5	1.914	256	259	267	BB	378220	4026217	0.22%	0.162%
6	8.359	1155	1172	1188	BB 4	156164	7380239	0.41%	0.297%
7	9.286	1266	1304	1306	BB	18524776	1801474848	100.00%	72.576%
8	9.377	1306	1317	1327	BB 2	245646	17878229	0.99%	0.720%
9	10.683	1488	1502	1555	BB	8598424	265582021	14.74%	10.700%

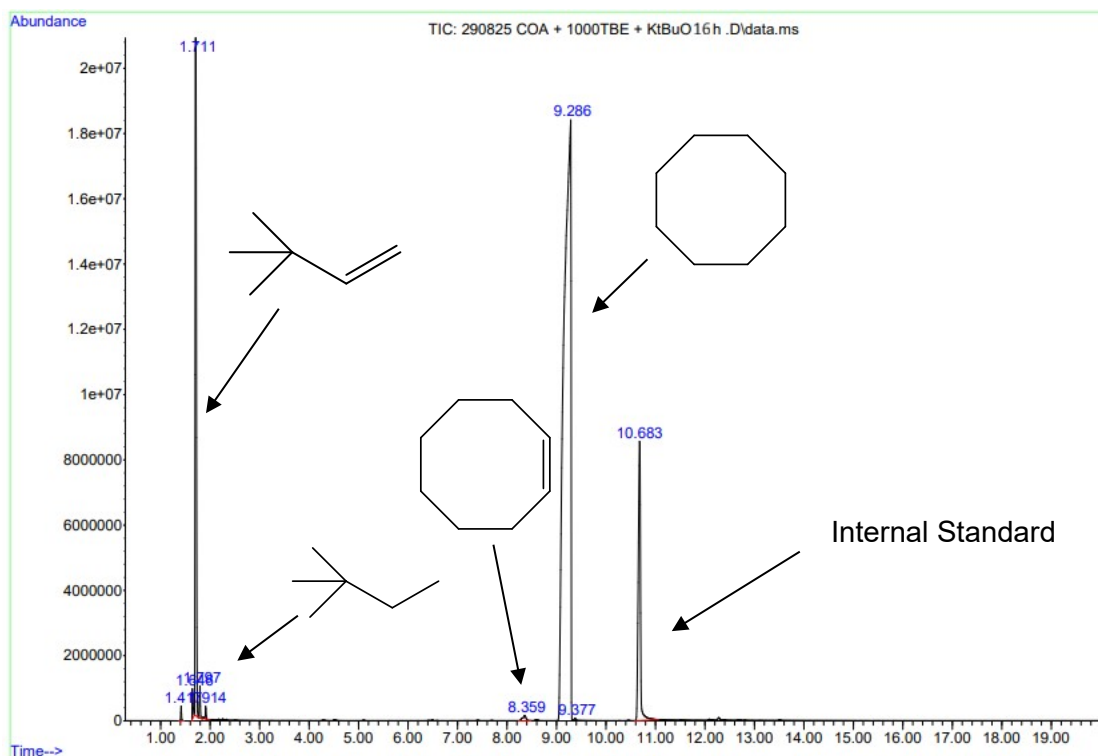


Figure 9: GC-MS spectra of COA (3.0 mmol), TBE (3.0 mmol), Ir2 (3.0 μ mol), and KO^tBu (15.0 μ mol) after 16h.

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.418	184	188	195	BB	247969	2568682	0.14%	0.111%
2	1.645	218	221	227	BB	1433195	20313636	1.12%	0.880%
3	1.714	227	230	238	BB	19914265	272722041	15.06%	11.820%
4	1.792	238	241	249	BB 2	620512	8707405	0.48%	0.377%
5	1.917	256	259	270	BB	187571	2097935	0.12%	0.091%
6	8.359	1158	1172	1193	BB 5	172844	11059769	0.61%	0.479%
7	9.344	1265	1312	1317	BB	16924503	1810582151	100.00%	78.472%
8	10.689	1488	1503	1555	BB	5990565	179237787	9.90%	7.768%

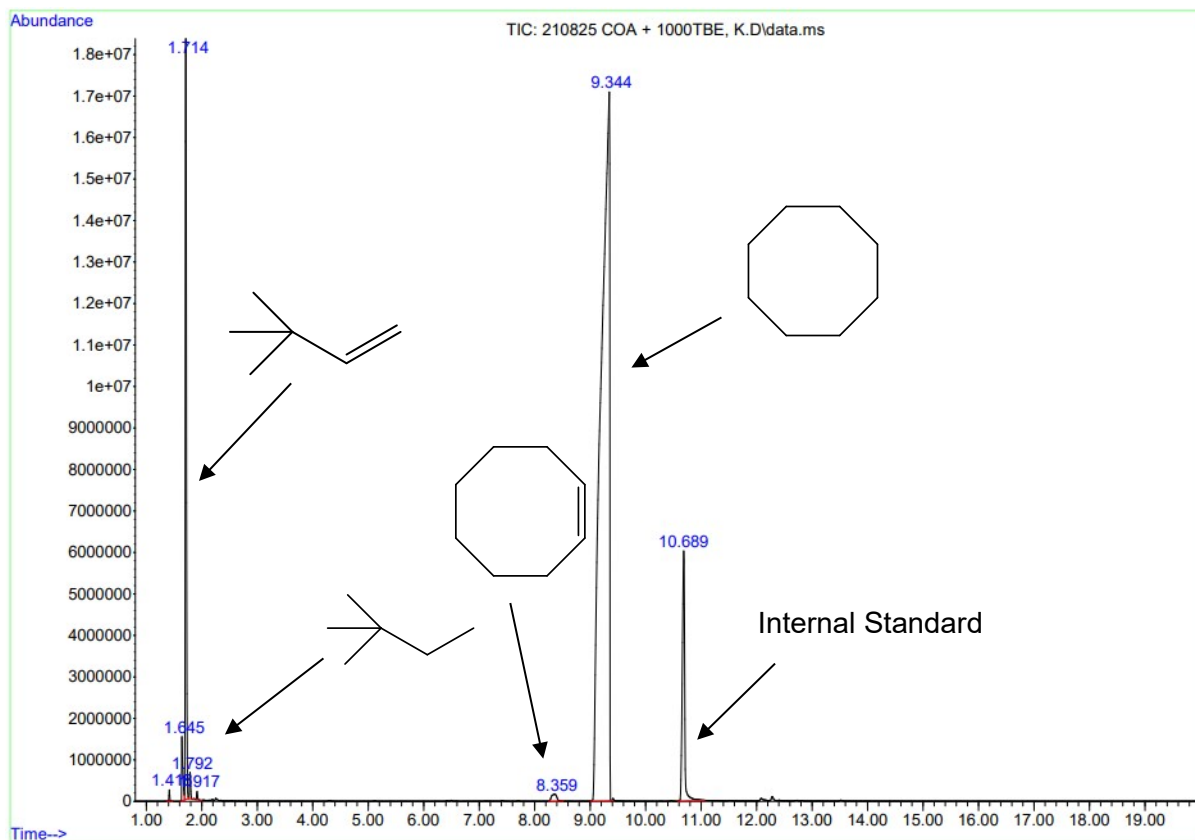


Figure 10: GC-MS spectra of COA (3.0 mmol), TBE (3.0 mmol), Ir2 (3.0 μ mol), and KO^tBu (15.0 μ mol) after 24h.

IV. Substrate scope study

GC-MS analysis was conducted to confirm product formation in the substrate scope study. Retention times and mass spectra matched expected values, with molecular ion peaks and key fragments consistent with the proposed products. Representative spectra are included.

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.645	218	221	226	BB	925875	10385977	0.31%	0.262%
2	1.711	226	230	238	BB	22884533	377124868	11.11%	9.510%
3	1.791	238	241	248	BB	1414683	15245427	0.45%	0.384%
4	10.661	1486	1498	1513	BB	5571061	144208069	4.25%	3.637%
5	16.738	2311	2360	2378	BB	26322548	3395787736	100.00%	85.636%
6	16.992	2388	2396	2408	BB	1058752	22611368	0.67%	0.570%

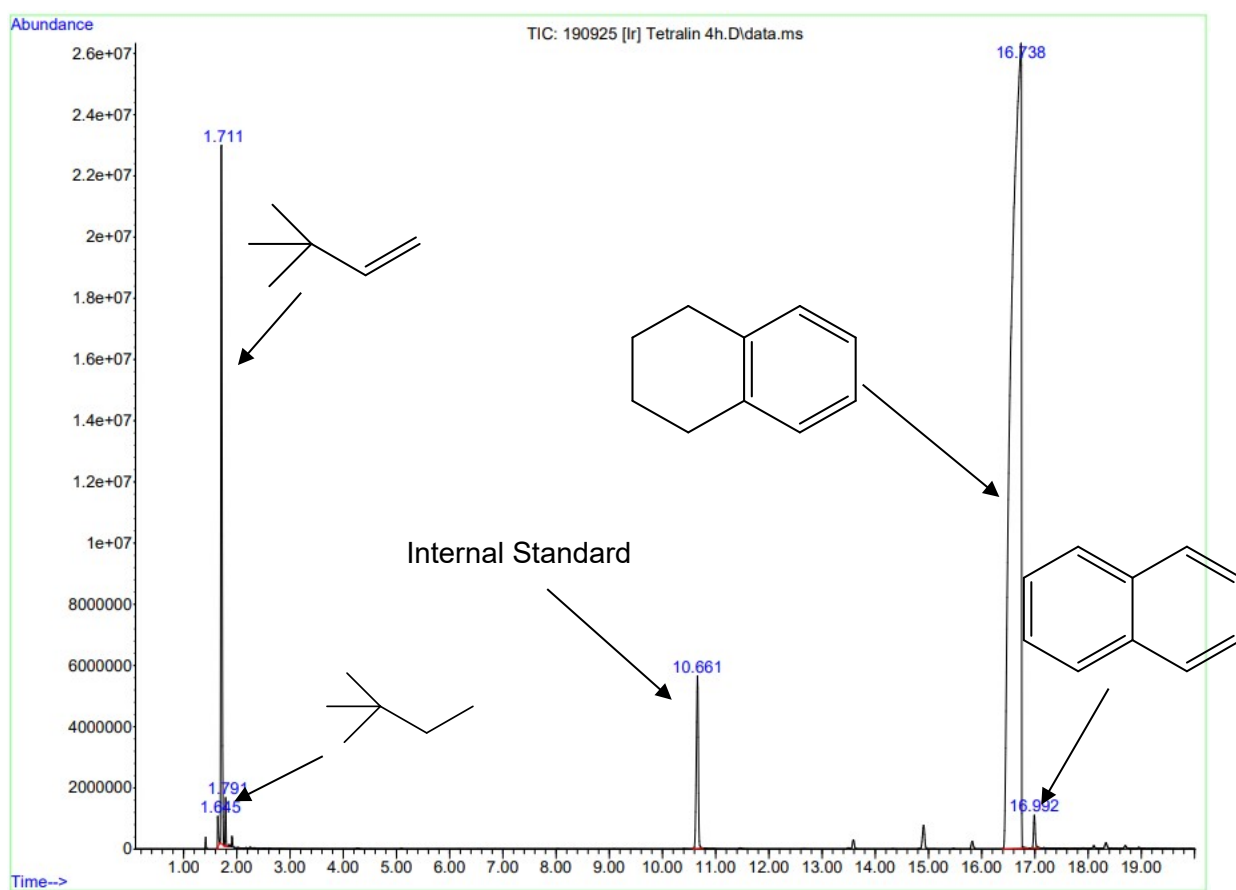


Figure 11: GC-MS spectra of tetralin (3.0 mmol), TBE (3.0 mmol), Ir2 (3.0 μ mol), and NaOtBu (15.0 μ mol).