Supporting Information for:

Synthesis of *p*-Xylene from Ethylene

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Materials and Methods

General Considerations

All manipulations were carried out under an inert atmosphere using an argon filled glove box or using standard Schlenk techniques. 1-Hexene was purchased from Aldrich and distilled over Na prior to use. Ethylene (99.95% polymer purity) was purchased from Airgas National Welders and used as received. (^{iPr4}anthraphos)Ir(C_2H_4) was synthesized according to literature methods.[1] Gas chromatographic analysis of reactions was conducted on an Agilent Technologies 6850 GC instrument fitted with a fused silica capillary column (100 m length × 0.25 mm ID × 0.50 μm film thickness) with the following method.

FID detector: Temp = 300 ºC

Initial Temperature: 40 ºC

Final Temperature: 250 ºC

Oven Program: 40 ºC, hold for 20 min

Ramp 1: 85 ºC/min to 150 ºC, hold for 5 min

Ramp 2: 10 ºC/min to 250 ºC, hold for 20 min

Products were confirmed using authentic samples and calibrated with an internal standard (mesitylene).

Typical procedure for iridium catalyzed disproportionation of 1-hexene. In an argon filled glovebox a 4 mL Kontes vial equipped with a Teflon screw-cap was charged with (^{iPr4}Anthraphos)Ir(C_2H_4) (8.5 mg, 0.0135 mmol) and dissolved in 1-hexene (2.5 g, 29.7 mmol), sealed and added to an oil bath at 180 ºC. At regular intervals, the reaction mixture was brought

to room temperature and an aliquot of the sample analyzed by GC. An aliquot of 90 μL of solution was combined with 10 μL of mesitylene as an internal standard.

Scale up procedure for iridium catalyzed disproportionation of 1-hexene. In an argon filled glovebox a 20 mL Kontes vial equipped with a Teflon screw-cap was charged with (^{iPr4}Anthraphos)Ir(C_2H_4) (10.7 mg, 0.017 mmol) and dissolved in 1-hexene (10.0 g, 118.8 mmol) sealed and added to an oil bath at 180 ºC. The reaction was monitored by GC analysis. When equilibrium had been reached the solution was cooled to room temperature and the volatiles separated from the iridium catalyst via vacuum transfer. To measure a maximum TON the remaining iridium catalyst was recharged with 1-hexene and the procedure repeated until the catalyst was recycled a total of three times. Total TON's observed: 7477.

Procedure for the Diels-Alder reaction of hexadienes mixture with ethylene. To a 22 mL stainless steel Parr reactor was added 5.0 g of crude solution isolated by vacuum transfer from the disproportionation. The vessel was sealed, then pressurized with ethylene to 600 psi and left at room temperature for 30 minutes in order for ethylene to saturate the solution. Once saturated, the vessel was sealed at a static pressure of 600 psi and heated to 250 ºC for 48 hours. Upon completion the reaction was cooled to room temperature and the contents of the vessel collected in a tared vial. 4.89 g of solution was isolated from the reaction. Some contents were lost due to the volatility of C6 hydrocarbons. An aliquot of this reaction mixture was taken and combined with a standard (mesitylene) and analyzed by GC. 96 % conversion was observed with respect to (2*E*, 4*E*) – hexadiene.

Procedure for the dehydrogenation of Diels-Alder adduct mixture. A Carbolite furnace with a quartz tube was filled with 1% wt Pt/Al_2O_3 (25g). To one end of the furnace tube was attached a glass trap with an oil bubbler. The other end was fitted with 14/20 ground glass joint and connected to a two-neck 50 mL round bottom flask. The second neck of the flask was fitted with a septum and N_2 was added to the system via a needle through this septum. The furnace was warmed to 400 ºC under an atmosphere of N_2 for 30 minutes to dry the catalyst. Following this preactivation, the glass collection trap was cooled with liquid N_2 and 2.0 mL of DA mixture added to the two neck flask. N_2 was purged through the solution at a rate of ca. 0.5 mL/second (1 bubble). Once the reaction began, the two-neck flask was slowly warmed to 70 ºC to ensure all the material was carried over the catalyst. When the reaction was complete (ca. 1hr) the contents of the trap were warmed and collected by washing with pentanes. Standard (mesitylene) was added and the solution analyzed by GC.

Procedure for one-pot HXD formation, Diels-Alder reaction. In an argon filled glovebox a 22 mL stainless steel Parr reactor was charged with (^{iPr4}Anthraphos)Ir(C_2H_4) (24.2 mg, 0.038 mmol) and dissolved in a mixture of 1-hexene (1.5 mL, 12.0 mmol) and mesitylene (1.5 mL, 10.8 mmol). The vessel was sealed, taken out of the glovebox, then pressurized with ethylene to 600 psi and left at room temperature for 30 minutes in order for ethylene to saturate the solution. Once saturated, the vessel was sealed at a static pressure of 600 psi and heated to 250 ºC for 24 hours. At 24 hour intervals the vessel was cooled to room temperature, and an aliquot removed for GC analysis. To do this, the vessel was depressurized, brought into an argon filled glovebox and an aliquot removed via syringe. The vessel was then recharged with ethylene as described above and heated to 250 ºC.

Computational Details

All calculations were performed using the Gaussian 09 program[2] (revision B.01) on a Linux cluster. The restricted wave function was used for the singlet ground state. The free energies were evaluated by the B3LYP functional[3,4] with triple-ζ 6-311G(d) basis set on all atoms following the geometry optimizations at the same level in the gas phase. In addition, compound methods G2[5] and CBS-QB3[6,7] were also used. Frequency calculations on the optimized structures confirmed the local minimum with no imaginary frequencies found.

The thermochemistry of cyclohexene dehydrogenation to benzene was calculated to calibrate the computational method. The G2 method showed minimal errors from the experimental data and was thus used in calculations for *cis*-3,6-dimethylcyclohexene dehydrogenation to p-xylene.

Full reference for 16:
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.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Revision B.01, Gaussian, Inc., Wallingford, CT, **2009.**

Selected gas chromatograms for 1-hexene disproportionation, Diels-Alder, dehydrogenation, and one-pot experiments

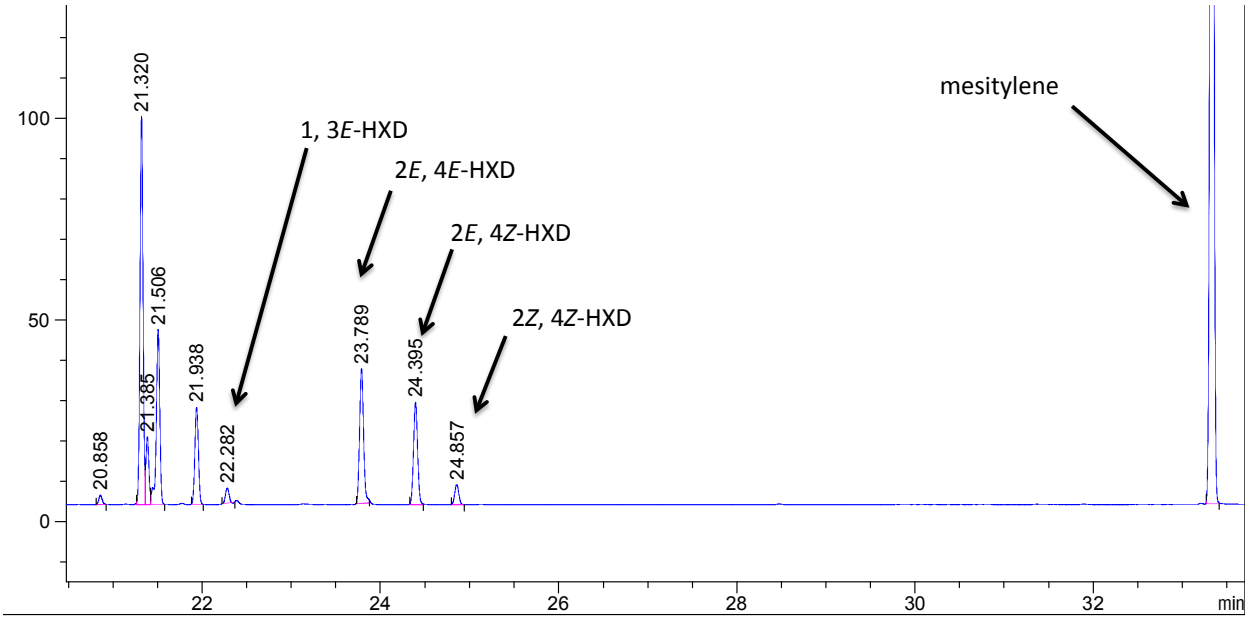

Fig. S1.

Gas chromatogram of 1-hexene disproportionation reaction

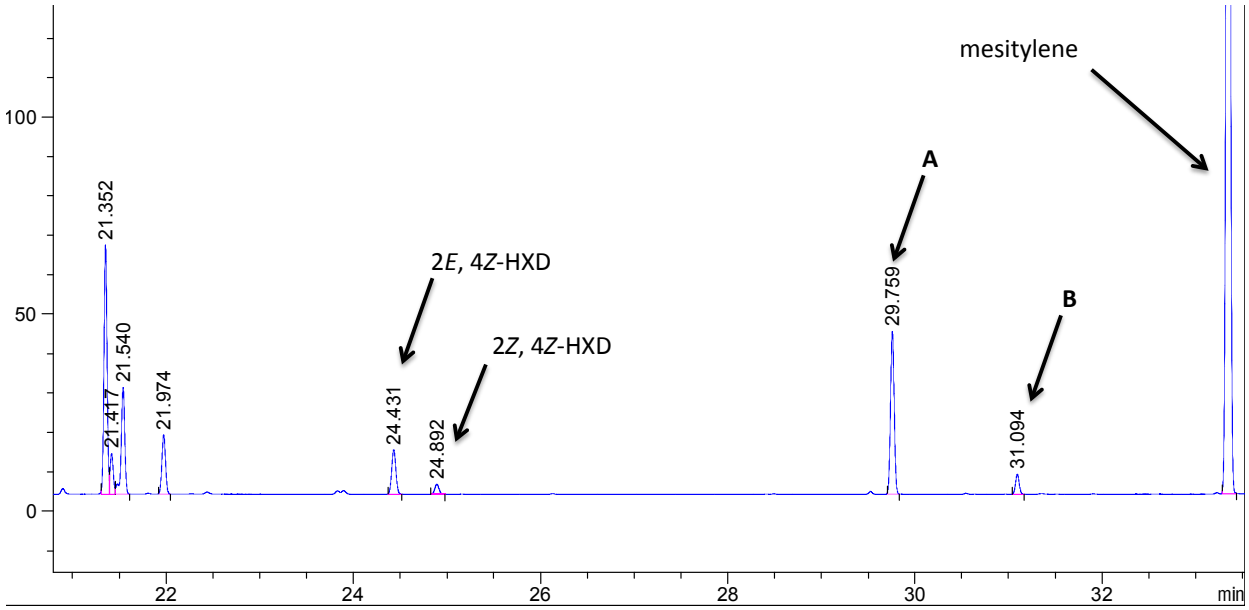

Fig. S2

Gas chromatogram of solution after Diels Alder reaction

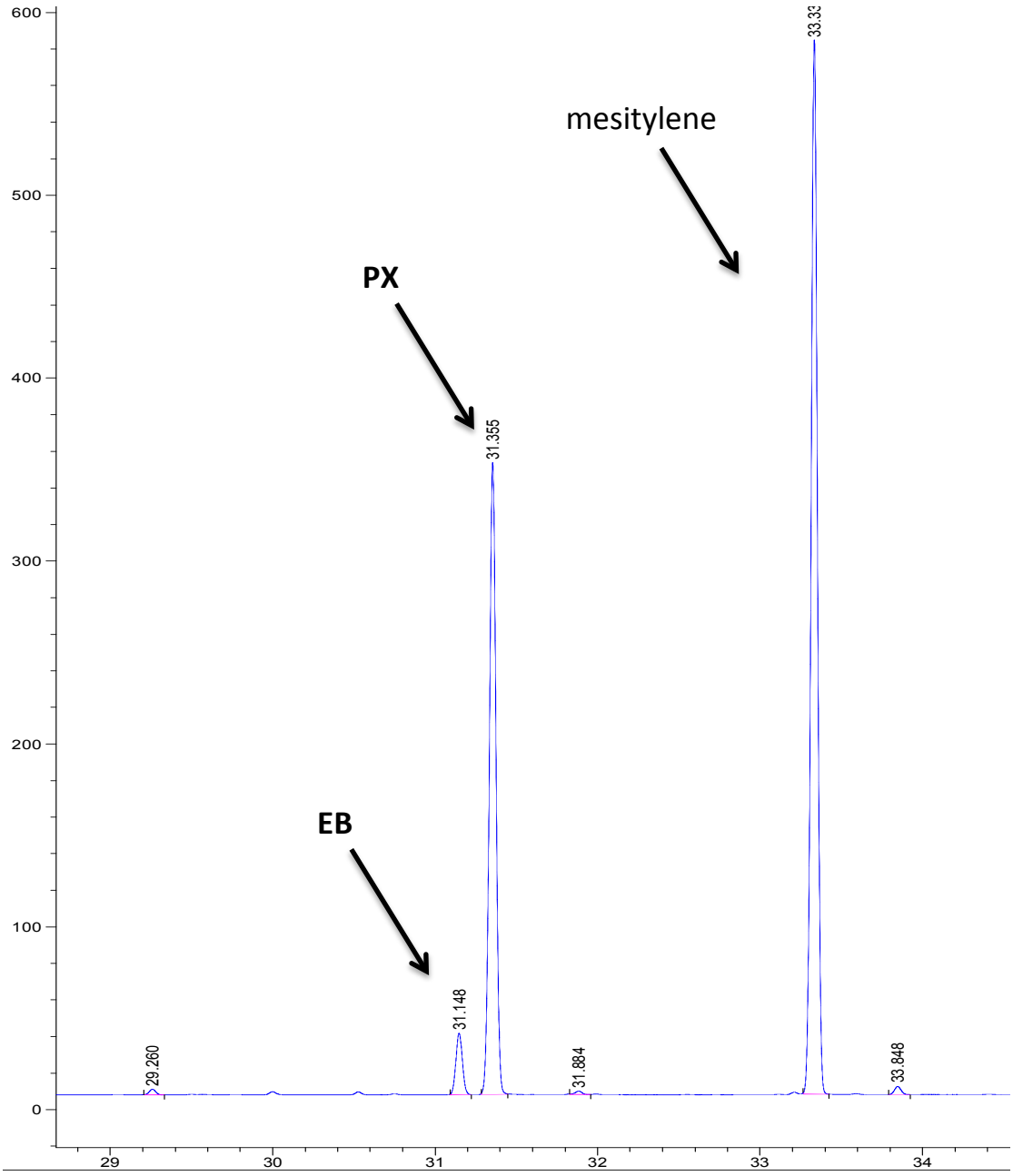

Figure S3. Gas Chromatogram of solution after dehydrogenation of Diels Alder solution.

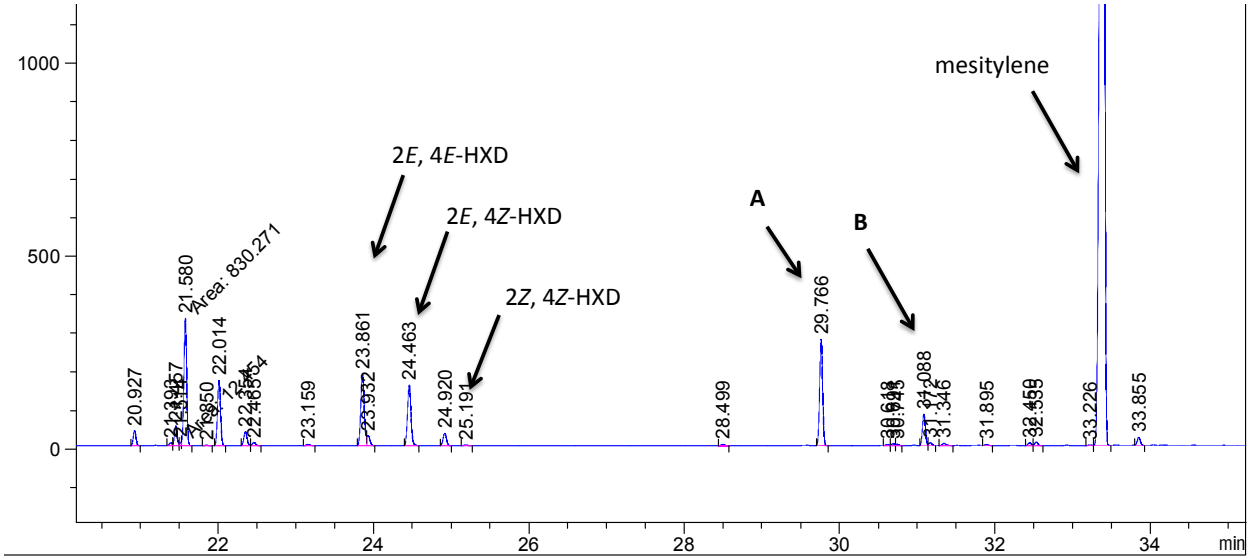

Figure S4. Gas chromatogram of one pot HXD formation, Diels-Alder reaction. (Table 2, entry 2)

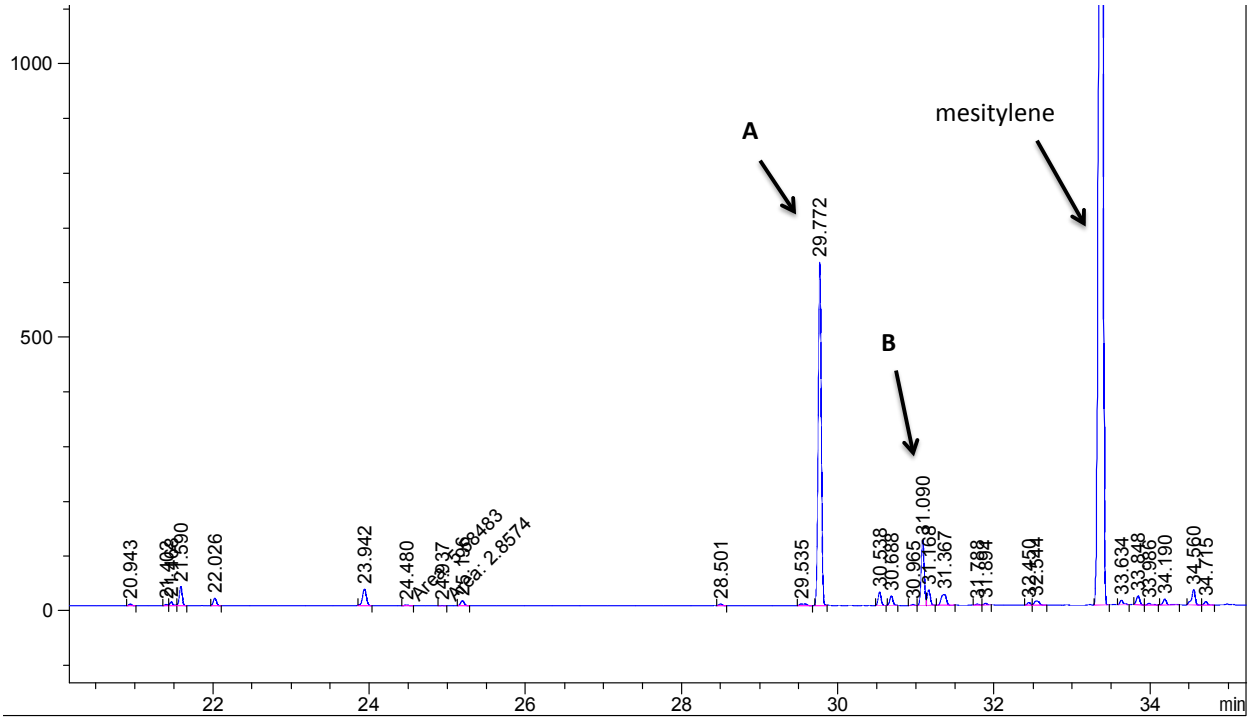

Figure S5. Gas chromatogram of one pot HXD formation, Diels-Alder reaction. (Table 2, entry 6)

Table S1. Thermodynamic data for C_6H_{10} -> 2 H_2 + C_6H_6 under 1atm at 298 K.

	ΔH° (kcal/mol)	ΔS° (e.u.)	ΔG° (kcal/mol)
Experimental	20.84	52.57	–
B3LYP/6-311G(d)	16.48	58.91	-1.09
G2	20.68	58.42	3.26
CBS-QB3	17.70	58.82	0.17

Table S2. Thermodynamic data by G2 method for C_8H_{14} -> 2 H_2 + C_8H_{10} under 1atm at various temperatures.

T (K)	ΔH° (kcal/mol)	ΔS° (e.u.)	ΔG° (kcal/mol)
298	18.38	60.27	0.41
523	20.80	63.85	-13.63
673	21.46	64.47	-23.26

Cartesian Coordinates of Optimized Structures

Hydrogen

B3LYP/6-311G(d)

H	0.00000000	0.00000000	0.37095000
H	0.00000000	0.00000000	-0.37095000

G2

H	0.00000000	0.00000000	0.36866600
H	0.00000000	0.00000000	-0.36866600

CBS-QB3

H	0.00000000	0.00000000	0.37196200
H	0.00000000	0.00000000	-0.37196200

Cyclohexene

B3LYP/6-311G(d)

C	-0.00527600	0.66660300	1.30513500
C	0.00527600	1.50074000	0.04849300
C	0.36909000	0.67201000	-1.19201600
C	-0.36909000	-0.67201000	-1.19201600
C	-0.00527600	-1.50074000	0.04849300
C	0.00527600	-0.66660300	1.30513500
H	0.14468200	1.23581400	-2.10326100
H	-0.97983900	1.97037100	-0.08648600
H	0.70809500	2.33450800	0.16483900
H	-0.01954100	1.20080800	2.25318800
H	-1.45050600	-0.48784200	-1.19795100
H	-0.14468200	-1.23581400	-2.10326100
H	-0.70809500	-2.33450800	0.16483900
H	0.97983900	-1.97037100	-0.08648600
H	0.01954100	-1.20080800	2.25318800
H	1.45050600	0.48784200	-1.19795100

G2

C	-0.00527900	0.67043600	1.29613100
C	0.00527900	1.49669800	0.04042000
C	0.38635500	0.65768700	-1.17748000
C	-0.38635500	-0.65768700	-1.17748000
C	-0.00527900	-1.49669800	0.04042000
C	0.00527900	-0.67043600	1.29613100
H	0.20140700	1.22007900	-2.09955400
H	-0.98492800	1.94939400	-0.11275900
H	0.70221800	2.33615000	0.15646100
H	-0.02287400	1.20235100	2.24633000

H	-1.46142800	-0.44071500	-1.14489600
H	-0.20140700	-1.22007900	-2.09955400
H	-0.70221800	-2.33615000	0.15646100
H	0.98492800	-1.94939400	-0.11275900
H	0.02287400	-1.20235100	2.24633000
H	1.46142800	0.44071500	-1.14489600

CBS-QB3

C	-0.00544000	0.66657100	1.30503900
C	0.00544000	1.50063700	0.04844900
C	0.36954500	0.67188200	-1.19234300
C	-0.36954500	-0.67188200	-1.19234300
C	-0.00544000	-1.50063700	0.04844900
C	0.00544000	-0.66657100	1.30503900
H	0.14513300	1.23571300	-2.10306800
H	-0.98023400	1.96862500	-0.08618600
H	0.70900900	2.33312300	0.16609600
H	-0.02000400	1.20010600	2.25217600
H	-1.45038500	-0.48579600	-1.19588700
H	-0.14513300	-1.23571300	-2.10306800
H	-0.70900900	-2.33312300	0.16609600
H	0.98023400	-1.96862500	-0.08618600
H	0.02000400	-1.20010600	2.25217600
H	1.45038500	0.48579600	-1.19588700

Benzene

B3LYP/6-311G(d)

C	-1.30229000	-0.49765900	-0.00000100
C	-1.08208500	0.87891700	-0.00000100
C	0.22010400	1.37651700	-0.00000600
C	1.30231100	0.49760400	0.00000000
C	1.08212200	-0.87887200	0.00000300
C	-0.22016200	-1.37650800	0.00000100
H	-2.31629700	-0.88513900	0.00000500
H	-1.92476000	1.56323100	0.00001200
H	0.39146500	2.44843900	0.00001300
H	2.31626900	0.88521400	0.00000500
H	1.92471200	-1.56329000	-0.00000200
H	-0.39138800	-2.44845100	-0.00000700

G2

C	1.27800600	-0.55982100	0.00000000
C	1.12382000	0.82687700	-0.00000300
C	-0.15418400	1.38669600	-0.00000300
C	-1.27800700	0.55981800	0.00000000
C	-1.12382200	-0.82687500	0.00000300

C	0.15418700	-1.38669600	0.00000300
H	2.27379400	-0.99601700	0.00000100
H	1.99947100	1.47115600	-0.00000500
H	-0.27432100	2.46717200	-0.00000600
H	-2.27379500	0.99601500	-0.00000100
H	-1.99947300	-1.47115500	0.00000500
H	0.27432300	-2.46717100	0.00000600

CBS-QB3

C	-1.15972800	-0.77337300	0.00000000
C	0.08996200	-1.39087800	-0.00000300
C	1.24965000	-0.61759900	-0.00000500
C	1.15971200	0.77339600	0.00000000
C	-0.08993400	1.39088000	0.00000400
C	-1.24966200	0.61757400	0.00000300
H	-2.06187600	-1.37510200	0.00000100
H	0.15990500	-2.47305000	-0.00000300
H	2.22175500	-1.09819900	-0.00000600
H	2.06189900	1.37506800	0.00000100
H	-0.15994500	2.47304700	0.00000600
H	-2.22173700	1.09823600	0.00000600

cis-Dimethyl cyclohexene

G2

C	-0.65087000	1.32562400	-0.32447800
C	-1.57380900	0.13905800	-0.35028200
C	-0.79723300	-1.13314400	-0.70447200
C	0.51857000	-1.21535500	0.06321800
C	1.44582000	-0.06284400	-0.31635200
C	0.68776700	1.23629400	-0.32191500
H	-1.41822900	-2.01645900	-0.51075500
H	-2.32280900	0.31301600	-1.13660000
H	-1.11728700	2.31086900	-0.29612900
H	0.32448900	-1.16996100	1.14245800
H	1.01797400	-2.17354100	-0.12578600
H	1.82362600	-0.24746400	-1.33490400
H	1.28099600	2.15155400	-0.31784700
H	-0.57600100	-1.13025000	-1.77956200
C	-2.33200200	0.01300800	0.97497200
H	-2.86493900	0.93965500	1.20993600
H	-3.06626500	-0.79774200	0.92708000
H	-1.64435200	-0.19224300	1.79986200
C	2.65097300	0.01535700	0.61946300
H	3.20895900	-0.92639400	0.61666100
H	3.33524200	0.81555000	0.32019600
H	2.32329600	0.21542200	1.64447400

p-Xylene
G2

C	-1.41762800	0.00001000	0.01978000
C	-0.69667200	-1.19832700	0.00704200
C	0.69665700	-1.19833600	-0.00704800
C	1.41762800	-0.00000800	-0.01978400
C	0.69667200	1.19833000	-0.00704900
C	-0.69665700	1.19833900	0.00704400
H	-1.23292100	-2.14603800	0.01559100
H	1.23289400	-2.14605300	-0.01560000
H	1.23292000	2.14604100	-0.01560200
H	-1.23289300	2.14605600	0.01559300
C	2.92247100	-0.00000500	0.00731600
H	3.30095800	0.00054400	1.03512600
H	3.32537300	-0.88516000	-0.49261800
H	3.32539000	0.88460900	-0.49356400
C	-2.92247100	0.00000000	-0.00730700
H	-3.32537500	0.88516900	0.49259900
H	-3.30096800	-0.00058900	-1.03511200
H	-3.32537800	-0.88459900	0.49361100

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