Supplementary Information

ESI-MS, DFT and Synthetic Studies on the H_2-Mediated Coupling of Acetylene: Insertion of C=X Bonds into Rhodacyclopentadienes and Brønsted Acid Cocatalyzed Hydrogenolysis of Organorhodium Intermediates

Vanessa M. Williams, Jong Rock Kong, Byoung Joon Ko, Yogita Mantri, Jennifer S. Brodbelt,* Mu-Hyun Baik,* and Michael J. Krische*

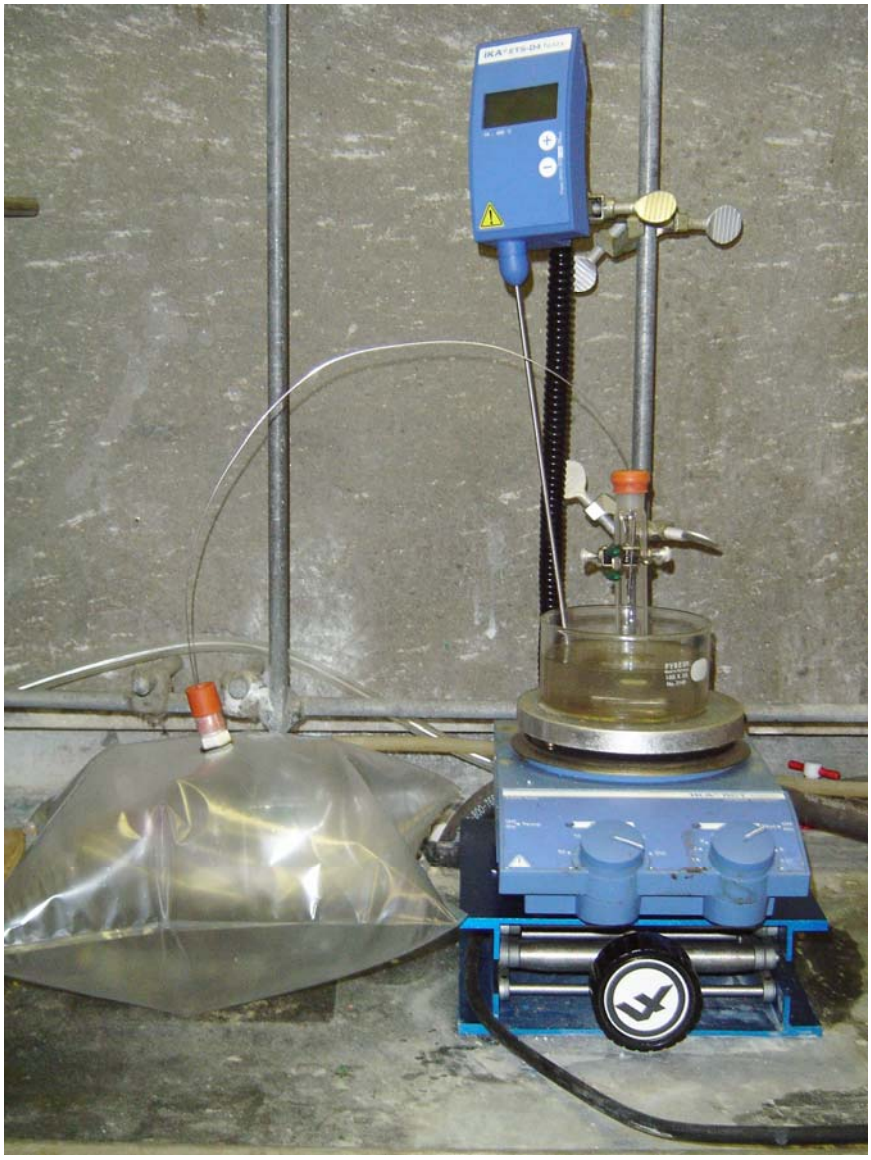
University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX 78712, USA
Indiana University, Department of Chemistry, Bloomington, IN 47405, USA
E-mail: jbrodbelt@mail.utexas.edu; mbaik@indiana.edu; mkrische@mail.utexas.edu

Experimental Section

General Experimental Details. All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred by oven-dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. Toluene was distilled from sodium and benzophenone. 1,2 Dichloroethane was distilled from calcium hydride. BIPHEP and *rac*-BINAP were used as received from Strem Chemicals. Triphenylacetic acid was used as received from Aldrich. Acetylene Gas was used as received from PRAXAIR (Atomic Absorption Grade). $[Rh(cod)_2]SbF_6$, and $[Rh(cod)_2]BARF$ were prepared in analogy with previously reported procedures.[1] Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F_{254}). Preparative column chromatography employing silica gel was performed according to the method of Still.[2] Solvents for chromatography are listed as volume: volume ratios. Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion [M + 1] or a suitable fragment ion. Melting points were obtained on a Thomas-Hoover Unimelt apparatus and are uncorrected. Proton nuclear magnetic resonance (H-NMR) spectra were recorded with a Varian Gemini (400 MHz or 300MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (C13-NMR) spectra were recorded with a Varian Gemini 300 (75 MHz) or 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. C13 NMR spectra were routinely run with broadband decoupling. Compounds **11a**, **11b**, and **12a**,[3] **14a**,[4] **15a**,[5] and *deuterio*-triethylsilane[6] were prepared according to the cited references and were consistent with literature characterization data.

[1] Guzel, B.; Omary, M.; Fackler, J.P., Jr.; Akegerman, A. *Inorg. Chim. Acta* **2001**, *325*, 45.
[2] Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
[3] Kong, J.-R.; Krische, M. J. *J. Am. Chem. Soc*. **2006**, *128*, 16041.
[4] Wang, X.; Bhatia P.A.; Daanen, J.F.; Latsaw, S.P.; Rohde, J.; Kolasa, T.; Hakeem, A.A.; Matulenko, M.A.; Nakane, M.; Uchic, M.E.; Miller, L.N.; Chang, R.; Moreland, R.B.; Brioni, J.D.; Stewart, A.O. *Bioorg. & Med. Chem.* **2005**, *13*, 4667.
[5] Yonezawa, Y.; Shin, C.; Ono, Y.; Yoshimura, J. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2905.
[6] Caseri, W.; Pregosin, P. S. *J. Organomet. Chem*. **1988**, *2*, 259.

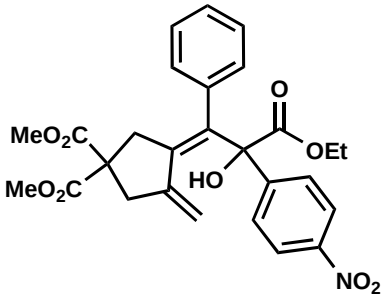
Experimental Apparatus



1) Reaction Vessel: 2.0 cm (Diameter) * 13.0 cm (Length)
2) Gas Bag: Tedlar® Gas Sampling Bag (Aldrich)
3) Cannula (Double-Tipped Needle): 24 in. (Length) – 20 (Gauge)

Preparation and Spectroscopic Data for Compounds.

Conversion of 12a to 12b. To an oven dried test tube (18 x 150 mm) equipped with stir bar and charged with $Rh(COD)_2SbF_6$ (5.5 mg, 0.01 mmol, 5 mol%), BIPHEP (5.3mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%), and Na_2SO_4 (58 mg, 0.4 mmol, 100 mol%) was added dichloroethane (1.2 mL), and stirred for 30 minutes at room temperature. A solution of **12a** (42mg, 0.2 mmol, 100 mol%) and carbonyl substrate **2a** (45.6 mg, 0.2 mmol, 100 mol%) in dichloroethane (0.8 mL, reaction is 0.1 M with respect to **2a**) was added to the reaction vessel under 1 atm of hydrogen. The mixture was stirred at 45 ^oC under 1 atm of hydrogen. After 24 hours, a solution of 1,6-diyne (42 mg, 0.2mmol, 100 mol%) in dichloroethane (1 mL) was added to the reaction vessel. The mixture was stirred at 45 ^oC under 1 atm of hydrogen for an additional 18 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, ethyl acetate: dichloromethane: hexanes, 1:6:12) to afford title compound **12b (**49.8 mg, 0.12 mmol) as a colorless oil in 58 % yield.



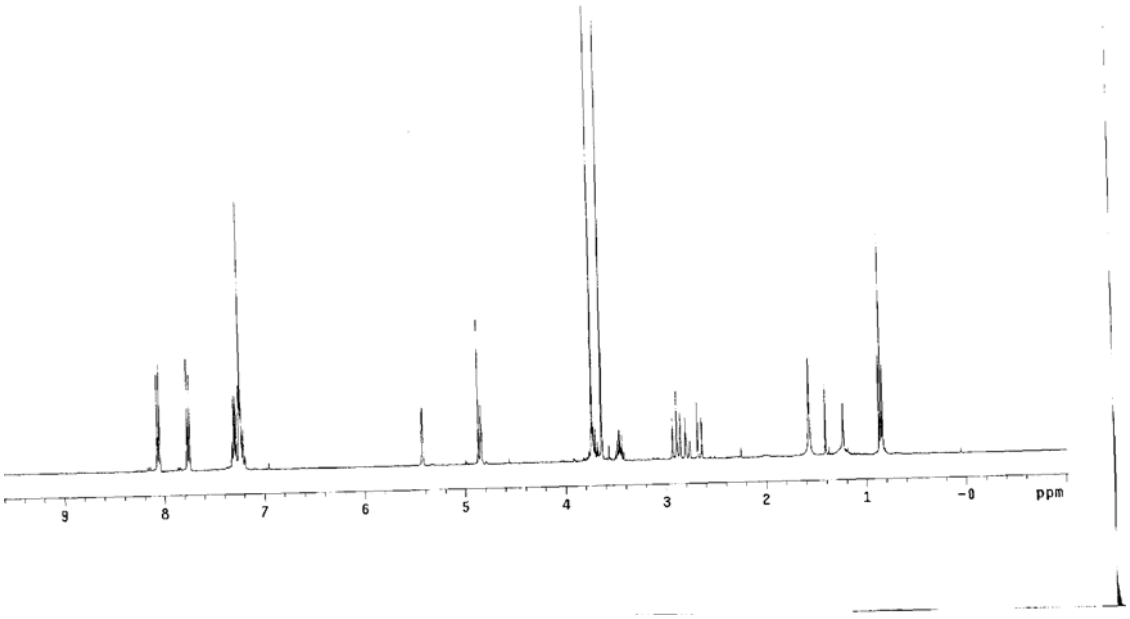
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 9.2 Hz, 2H), 7.32-7.19 (m, 5H), 5.43 (s, 1H), 4.86 (s, 1H), 4.84 (s, 1H), 3.78 (s, 3H), 3.76-3.68 (m, 1H), 3.64 (s, 3H), 3.50-3.42 (m, 1H), 2.91 (d, *J* = 16.8 Hz, 1H), 2.87 (d, *J* = 14.0 Hz, 1H), 2.78 (d, *J* = 15.6 Hz, 1H), 2.66 (d, *J* = 16.8 Hz, 1H), 0.85 (t, *J* = 7.2 Hz, 3H).

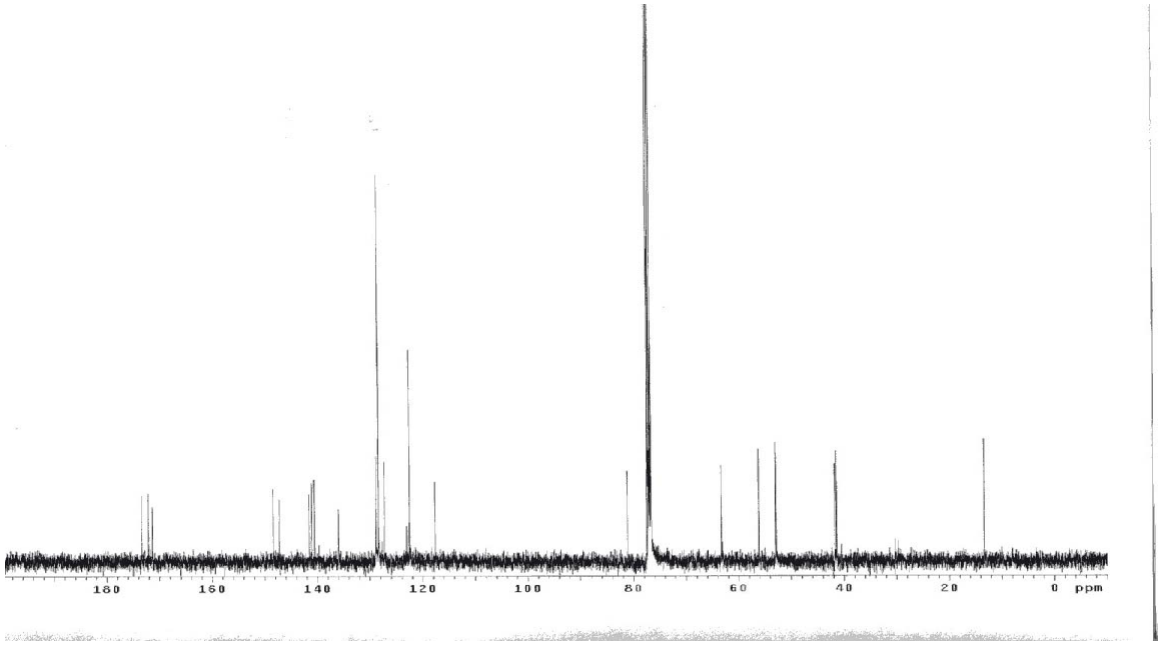
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 172.0, 171.3, 148.3, 147.2, 141.5, 141.0, 140.5, 135.9, 128.8, 128.3, 127.2, 123.0, 122.5, 117.6, 81.1, 63.2, 56.1, 52.9, 52.8, 41.7, 41.4, 13.3.

HRMS (CI): Calcd. For $C_{14}H_{23}NO_5$ [M+1]: 286.1654, Found: 286.1654.

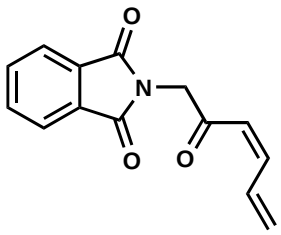
FTIR (neat): 3467, 2991, 2949, 2948, 2844, 1730, 1596, 1519, 1488, 1437, 1341, 1242, 1203, 1173, 1134, 1078.

R_f = 0.2 ethyl acetate: dichloromethane: hexanes, 1:6:12.


9
8
7
6
5
4
3
2
1
-0
ppm


180
160
140
120
100
80
60
40
20
0 ppm

Procedure for preparation of (*Z*)-2-(2-oxohexa-3,5-dienyl)isoindoline-1,3-dione (14b). To an oven dried test tube (18 x 150 mm) equipped with stir bar and charged with aldehyde **14a** (38 mg, 0.2 mmol, 100 mol%), *rac*-BINAP (6.2 mg, 0.01 mmol, 5 mol%), and $Rh(COD)_2BARF$ (11.8 mg, 0.01 mmol, 5 mol%) was added dichloroethane (2.0 mL, 0.1 M with respect to **14a**). The resulting solution was sparged with argon for 1 minute and acetylene was introduced to the reaction vessel using a balloon with 20G needle. The mixture was heated to 45 ^oC for 18 hours, at which point the reaction mixture was allowed to cool to room temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: ethyl acetate: hexanes, 15:85) to furnish **14b** (27 mg, 0.11 mmol) as a cream colored solid in 52% yield.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.86 (m, 2H), 7.77-7.72 (m, 2H), 7.64-7.51 (m, 1H), 6.58 (t, *J* = 11.18 Hz, 1H), 6.11 (d, *J* = 11.18 Hz, 1H), 5.63 (d, *J* = 17.8 Hz, 1H), 5.59 (d, *J* = 10.3 Hz, 1H), 4.76 (s, 2H).

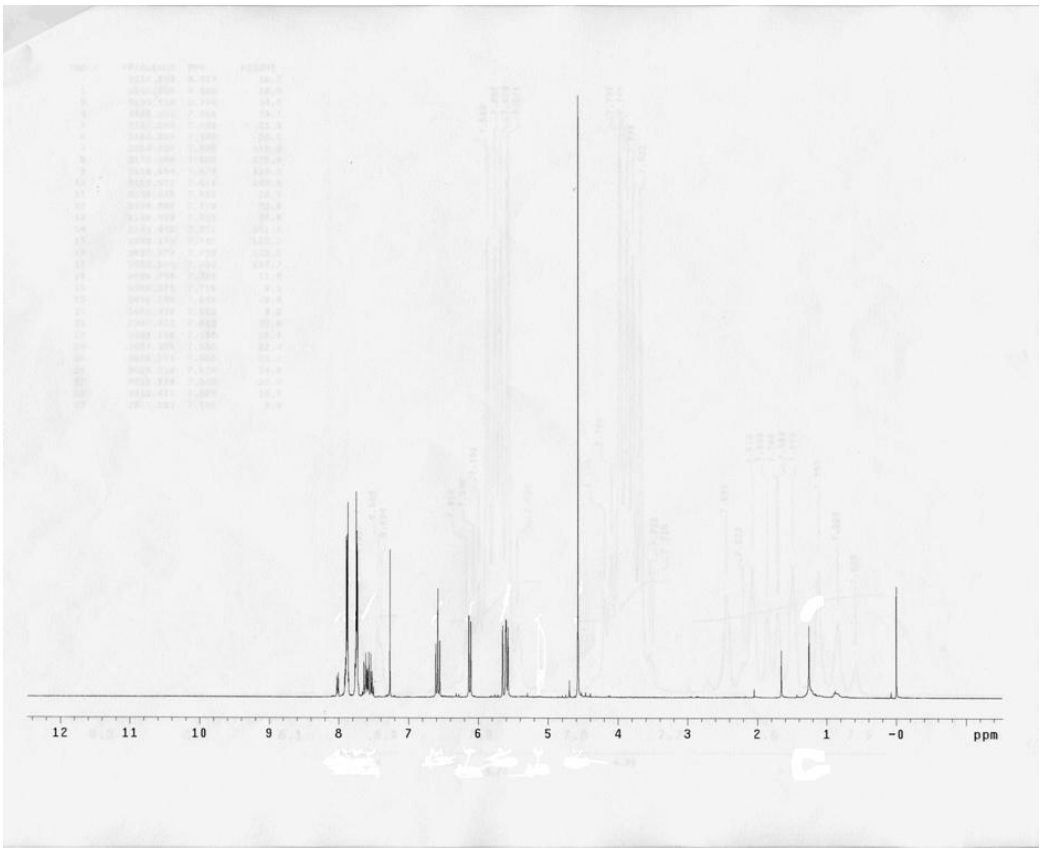
^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5, 167.7, 145.6, 134.1, 132.1, 128.9, 128.1, 123.5, 120.6, 47.5.

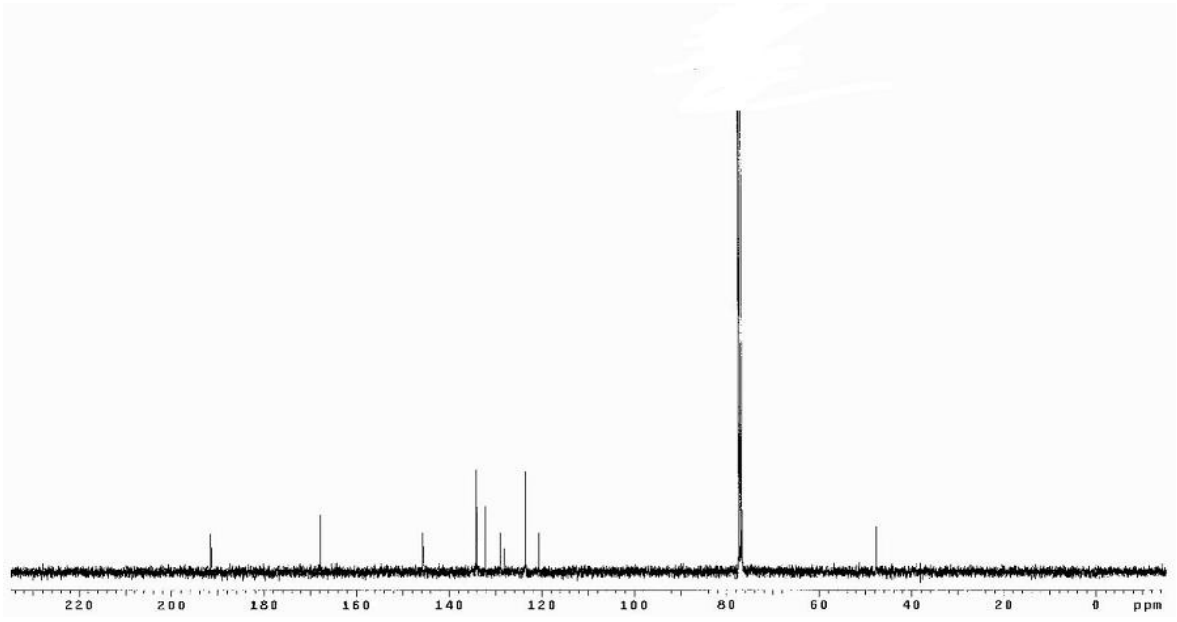
HRMS (CI): Calcd. for $C_{14}H_{12}NO_3$ [M+1]: 242.0817, Found: 242.0821.

FTIR (neat): 2926, 2848, 1751, 1714, 1695, 1413, 1387, 1308, 1088, 945, 712 cm^{-1}.

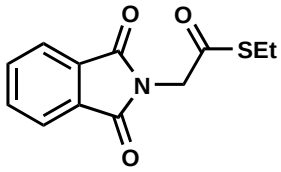
M.P.: 100 – 102 ^oC (crystals from ethyl acetate: hexanes).

R_f: 0.46 ethyl acetate:hexanes, 1:1.


12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm


220
200
180
160
140
120
100
80
60
40
20
0
ppm

Procedure for the preparation of (*S*)-ethyl 2-(1,3-dioxoisoindolin-2-yl)ethanethioate). In accordance with the method of Steglich,[3] to a 50 mL round bottomed flask equipped with stir bar and charged with *N*,*N*-phthalimidoglycine (2.05 g, 10 mmol, 100 mol%) was added dichloromethane (10 mL, 1 M) followed by 4-*N*,*N*-dimethylaminopyridine (75 mg, 0.5 mmol, 5 mol%). The solution was cooled to 0 ^{o}C and ethanethiol (2.16 mL, 30 mmol, 300 mol %) was added followed by dicyclohexylcarbodiimide (1.77 g, 10 mmol, 100 mol %). The mixture was allowed to stir at 0 ^{o}C for 5 minutes, at which point the reaction vessel was allowed to warm to room temperature. After 3 hours, the reaction mixture was filtered with the aid of dichloromethane (50 mL) and the filtrate was concentrated *in vacuo*. The oily residue was purified by flash column chromatography (SiO_2: neat dichloromethane) to furnish the thioester (1.27 g, 5.1 mmol) as colorless crystals in 51% yield.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.89 (m, 2H), 7.79-7.75 (m, 2H), 4.49 (s, 2H), 2.94 (q, J = 7.56 Hz, 2H), 1.26 (t, J = 7.56 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 167.3, 134.3, 131.8, 123.6, 46.5, 23.3, 14.4.

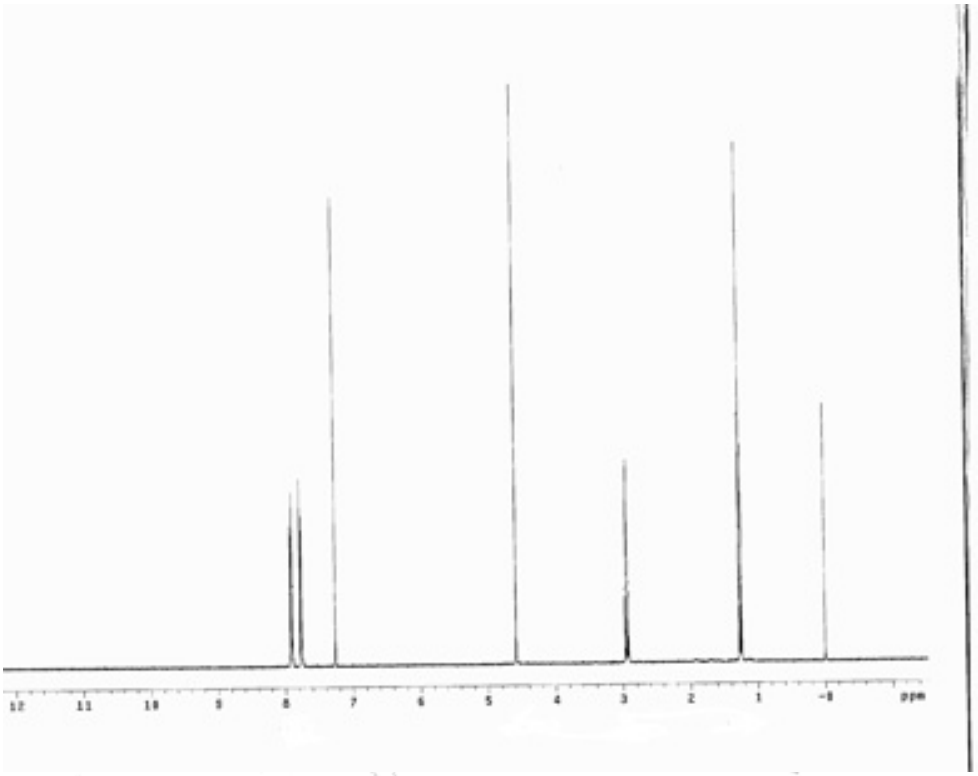
HRMS (CI): Calcd. for $C_{12}H_{12}NO_3S$ [M+1]: 250.0534, Found: 250.0538.

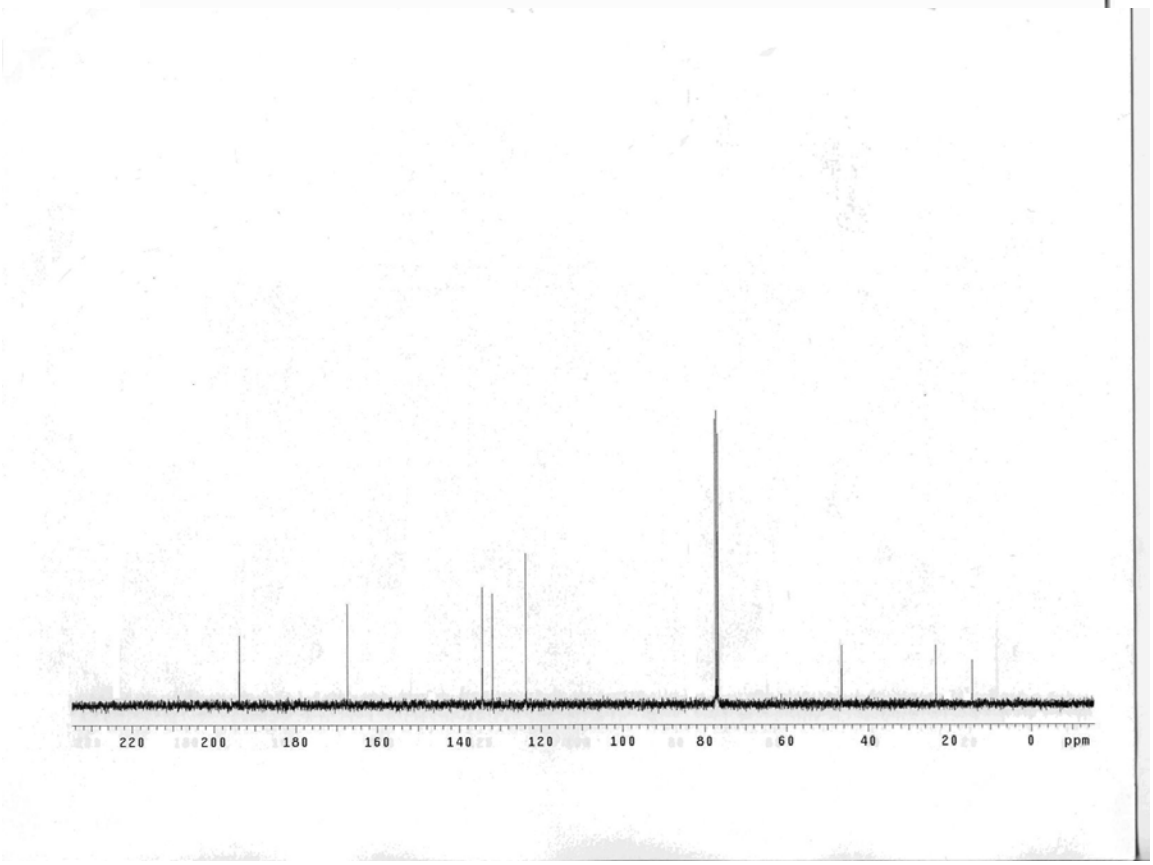
FTIR (neat): 3031, 2974, 2360, 1776, 1708, 1609, 1311, 1198, 1085, 927, 715 cm^{-1}.

M.P.: 117 – 119 ^{o}C (crystals from dichloromethane: hexanes).

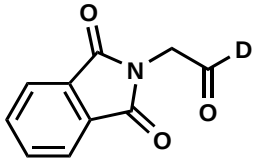
R_f: 0.34 ethyl acetate: hexanes, 1:3.

[3] Neises, B.; Steglich, W. *Angew. Chem. Int. Ed.* **1978**, *17*, 522.


12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm


220
200
180
160
140
120
100
80
60
40
20
0
ppm

Procedure for the preparation of 2-(1,3-dioxoisoindolin-2-yl)-*deuterio*-acetaldehyde (deuterio-14a). In accordance with Fukuyama's protocol,[4] to a 10 mL round bottomed flask equipped with stir bar and charged with thioester (150 mg, 0.6 mmol, 100 mol%) was added acetone (1.2 mL, 0.5 M) followed by Pd/C (3.2 mg, 10% wt. on carbon, 0.03 mmol, 5 mol%) and *deuterio*-triethylsilane (0.25 mL, 1.5 mmol, 250 mol%). The reaction mixture was allowed to stir for 12 hours at room temperature under an argon atmosphere, at which point the reaction mixture was filtered through celite with the aid of acetone (100 mL). The filtrate was concentrated *in vacuo* and the oily residue was purified by column chromatography (SiO_2: ethyl acetate: hexanes, 25:75) to furnish *deuterio*-**14b** (89 mg, 0.48 mmol) as ivory crystals in 79% yield.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, J = 5.47 Hz, 2H), 7.77 (dd, J = 5.47 Hz, 2H), 4.57 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2 (t, $J_{D\text{-}C}$ = 27.9 Hz) 167.5, 134.3, 131.9, 123.6, 47.2.

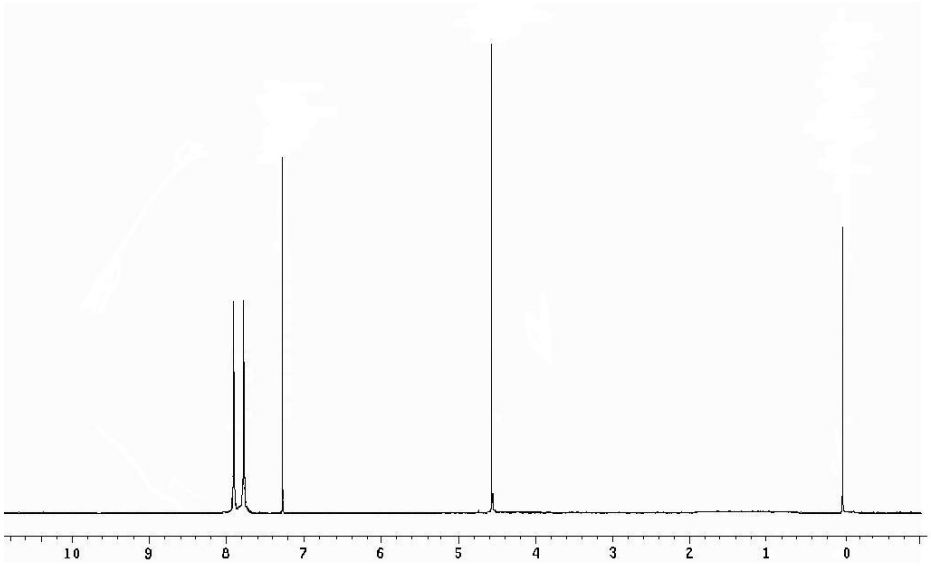
HRMS (CI): Calcd. for $C_{10}NO_3H_7D$ [M+1]: 191.0567, Found: 191.0571.

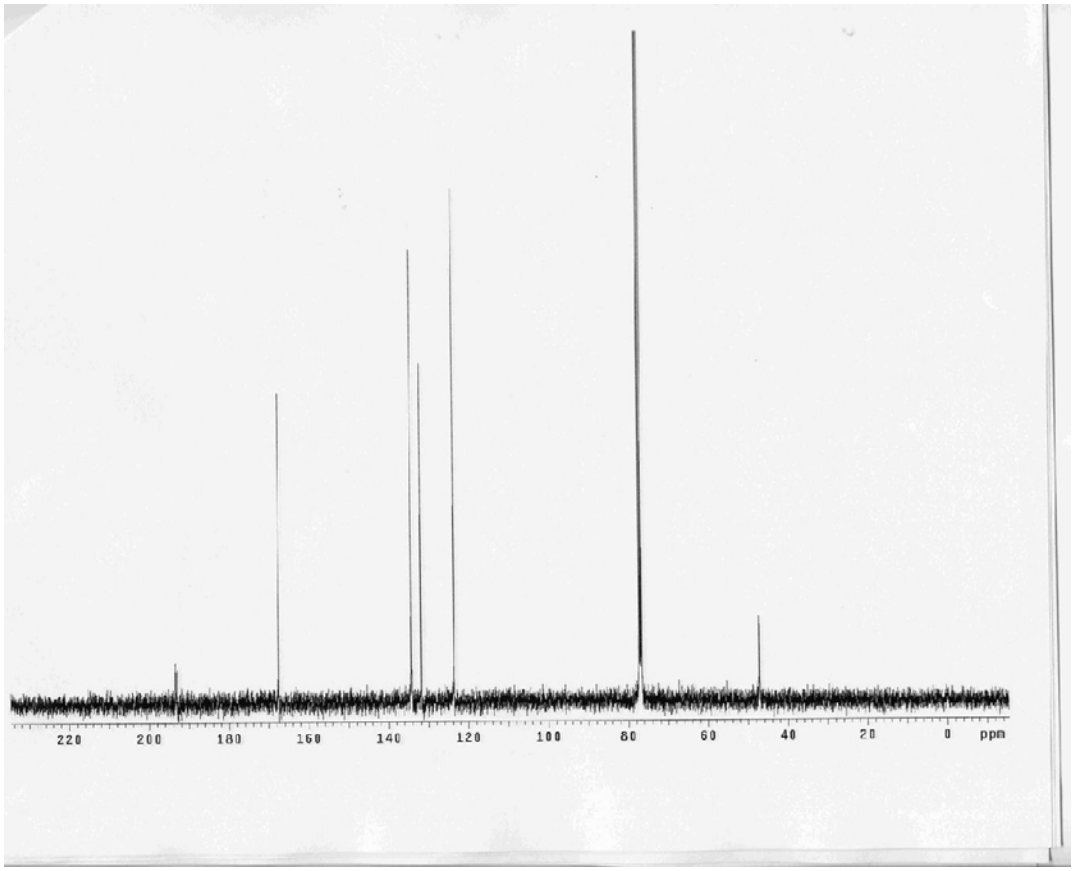
FTIR (neat): 3174, 2823, 1774, 1703, 1405, 714 cm^{-1}.

M.P.: 108 – 110 ^oC (crystals from ethyl acetate: hexanes).

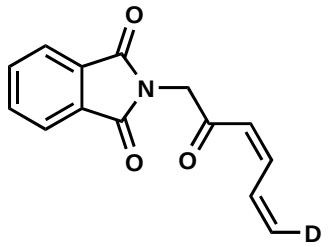
R_f: 0.2 ethyl acetate: hexanes, 1:1.

[4] (a) Tokuyama, H.; Fukuyama, T. *Aldrichimica Acta* **2004**, *37*, 87. (b) Fukuyama, T.; Lin, S. C.; Li, L. *J. Am. Chem. Soc*. **1990**, *112*, 7050.


10
9
8
7
6
5
4
3
2
1
0


220
200
180
160
140
120
100
80
60
40
20
0
ppm

(*Z*)-2-(2-oxohexa-3,5-dienyl-6-*deuterio*)isoindoline-1,3-dione (*deuterio*-14b). The title compound was prepared from *deuterio*-**6a** in analogy to the procedure described for the conversion of **14a** to **14b**.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.87 (m, 2H), 7.77-7.72 (m, 2H), 7.64-7.50 (m, 1H), 6.58 (t, *J* = 11.18 Hz, 1H), 6.11 (d, *J* = 11.18 Hz, 1H) 5.60 (d, *J* = 9.8 Hz, 1H), 4.76 (s, 2H).

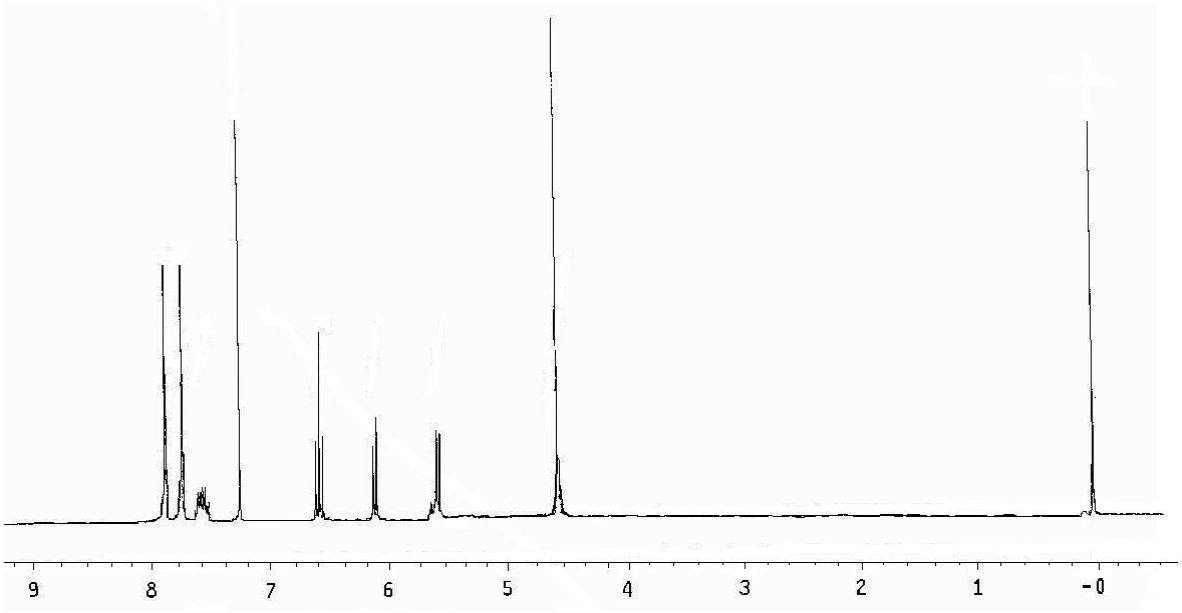
^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5, 167.7, 145.6, 134.1, 132.9, 128.9, 128.1, 123.5, 120.6, 47.5.

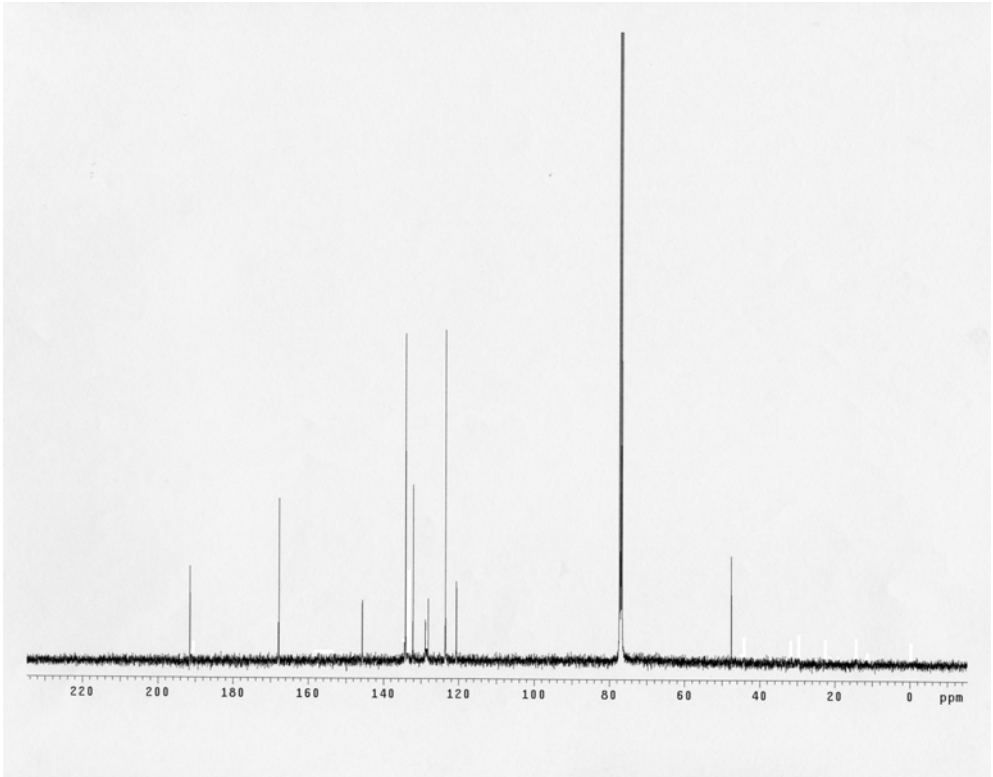
HRMS (CI): Calcd. for $C_{14}H_{11}DNO_3$ [M+1]: 242.0817, Found: 242.0821.

FTIR (neat): 2923, 2847, 1746, 1712, 1692, 1409, 1388, 1303, 1090, 943, 711 cm^{-1}.

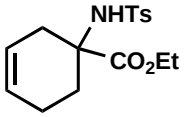
M.P.: 102-104 ^{o}C (crystals from ethyl acetate: hexanes).

R_f: 0.46 ethyl acetate: hexanes, 1:1.


9
8
7
6
5
4
3
2
1
-0


220
200
180
160
140
120
100
80
60
40
20
0
ppm

Conversion of 15a to 15b and *iso*-15b. To an oven tried test tube (18 x 150 mm) equipped with stir bar and charged with $MgSO_4$ (48mg, 0.4 mmol, 200 mol %), triphenyl acetic acid (2.88 mg, 0.01 mmol, 5 mol %), BIPHEP (5.23 mg, 0.01 mmol, 5 mol%) and $Rh(COD)_2SbF_6$ (5.55 mg, 0.01 mmol, 5 mol%) was added 1,2-dicholoroethane (0.4 mL). The resulting solution was sparged with argon for 1 minute, at which point substrate **15a** (54 mg, 0.2 mmol, 100 mol%) was added as a solution in dichloromethane (0.27 mL, 0.3 M overall concentration with respect to **15a**) *via* syringe. A gas bag filled with approximately equal volumes of C_2H_2 and H_2 was attached to the reaction vessel using a cannula. The reaction vessel was sparged with the C_2H_2/H_2 mixture and the reaction mixture was allowed to stir at 45 ^oC for 24 hours, at which point the reaction mixture was deposited directly onto a silica gel column. Purification by column chromatography (SiO_2: ethyl acetate: hexanes, 20:80) followed by recrystallization from dichloromethane: hexanes provides compound **15b** and *iso*-**15b** (50 mg, 0.15 mmol) as a colorless crystalline solid in 75% yield as a 4:1 mixture of alkene isomers. Spectroscopic data corresponds to the major isomer. See S3 for apparatus setup.



^{1}H NMR (400MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.55 Hz, 2H), 7.27 (d, *J* = 8.55 Hz, 2H), 5.65 – 5.59 (m, 1H), 5.41 – 5.38 (m, 1H), 5.06 (s, 1H), 4.05 – 3.98 (m, 2H), 2.59 (dt, *J* = 17.78, 5.13 Hz, 1H), 2.24 (s, 3H), 2.8 (dt, *J* = 17.78, 4.1 Hz, 1H), 2.11 – 1.88 (m, 4H), 1.21 (t, *J* = 7.18 Hz, 3H).

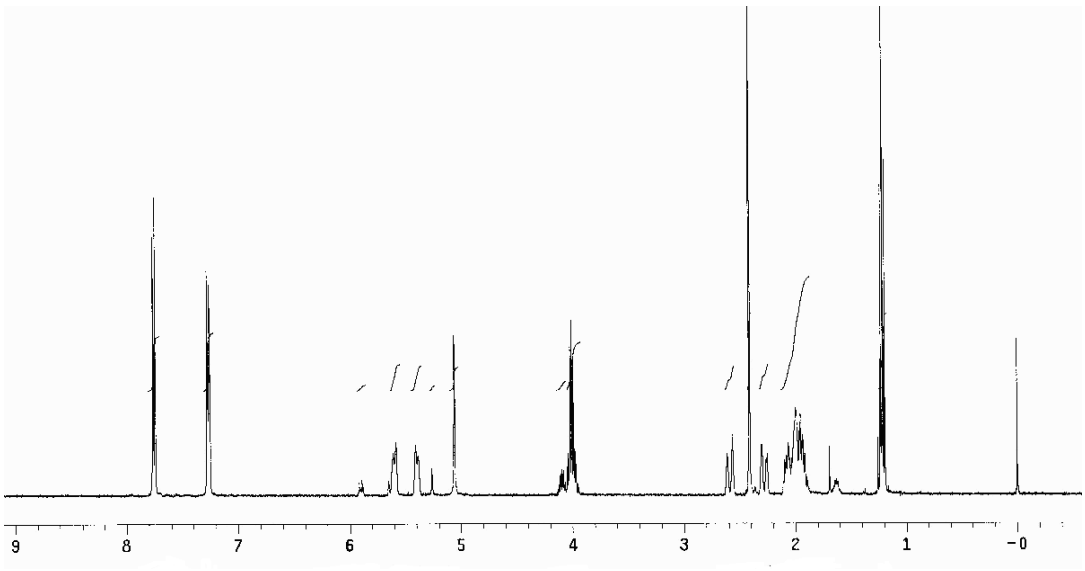
^{13}C NMR (100MHz, $CDCl_3$): δ 172.1, 142.2, 139.9, 129.2, 126.2, 125.5, 122.9, 60.4, 58.9, 32.7, 29.6, 21.4, 20.9, 13.7.

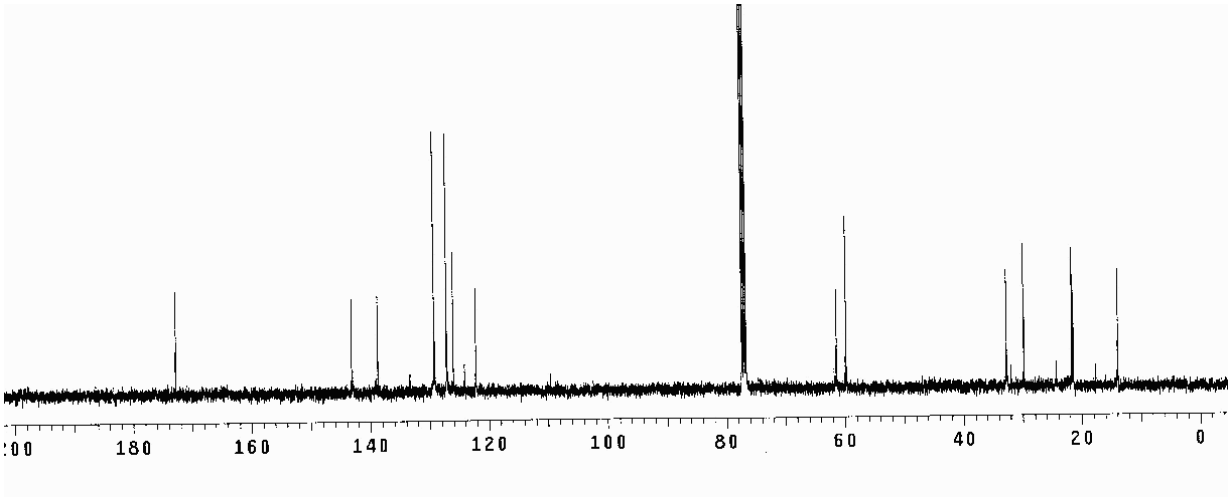
HRMS (CI): Calcd. for $C_{16}H_{22}NO_4S$ 324.1270 [M+1], Found: 324.1264.

FTIR (neat):3273, 2996, 2924, 2778, 1732, 1447, 1320, 1247, 1155, 1041, 818, 666 cm^{-1}.

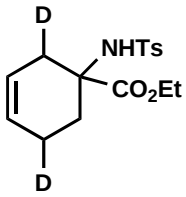
MP: 104 – 107 ^oC (crystals from dichloromethane: hexanes).

R_f : 0.25 in neat dichloromethane.


9
8
7
6
5
4
3
2
1
-0


180
160
140
120
100
80
60
40
20
0

***deuterio*-15b.** The title compound was prepared from **15a** in analogy to the procedure described for the conversion of **15a** to **15b** but using deuterium gas.



^{1}H NMR (400MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.55 Hz, 2H), 7.27 (d, *J* = 8.55 Hz, 2H), 5.65 – 5.59 (m, 1H), 5.41 – 5.38 (m, 1H), 5.06 (s, 1H), 4.05 – 3.98 (m, 2H), 2.59 (dt, *J* = 17.78, 5.13 Hz, 0.6H), 2.24 (s, 3H), 2.8 (dt, *J* = 17.78, 4.1 Hz, 0.4H), 2.11 – 1.88 (m, 3H), 1.21 (t, *J* = 7.18 Hz, 3H).

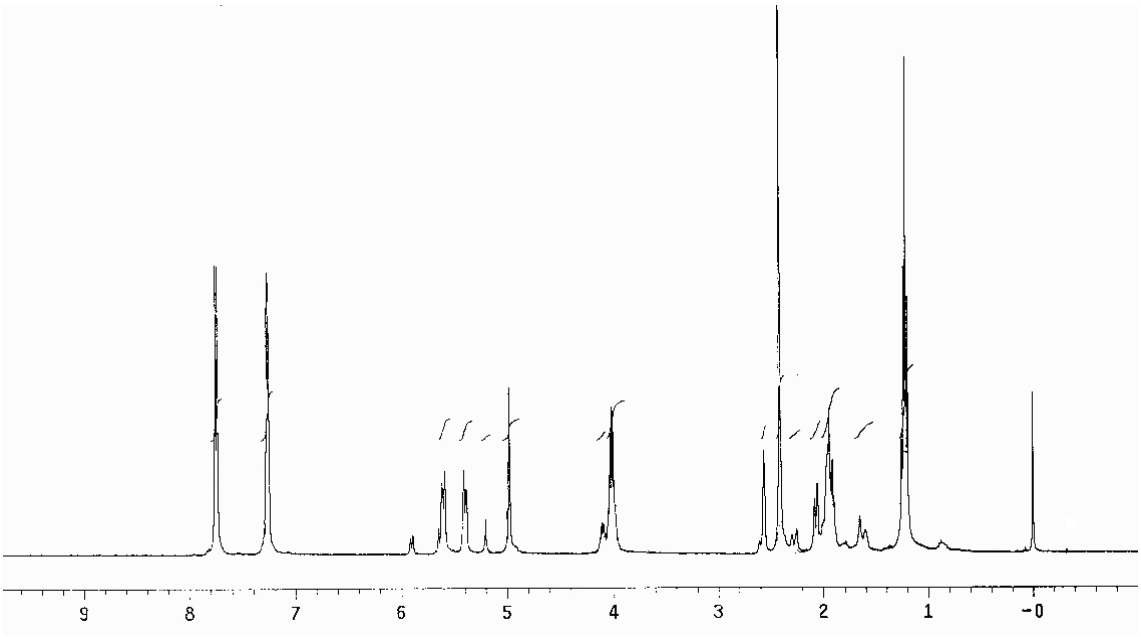
^{13}C NMR (100MHz, $CDCl_3$): δ 172.9, 143.2, 138.7, 129.3, 127.2, 126.1, 122.2, 61.4, 59.7, 32.8 (t, J = 28.7 Hz), 29.7, 22.8 (t, *J* = 27.2 Hz) 21.5, 13.9.

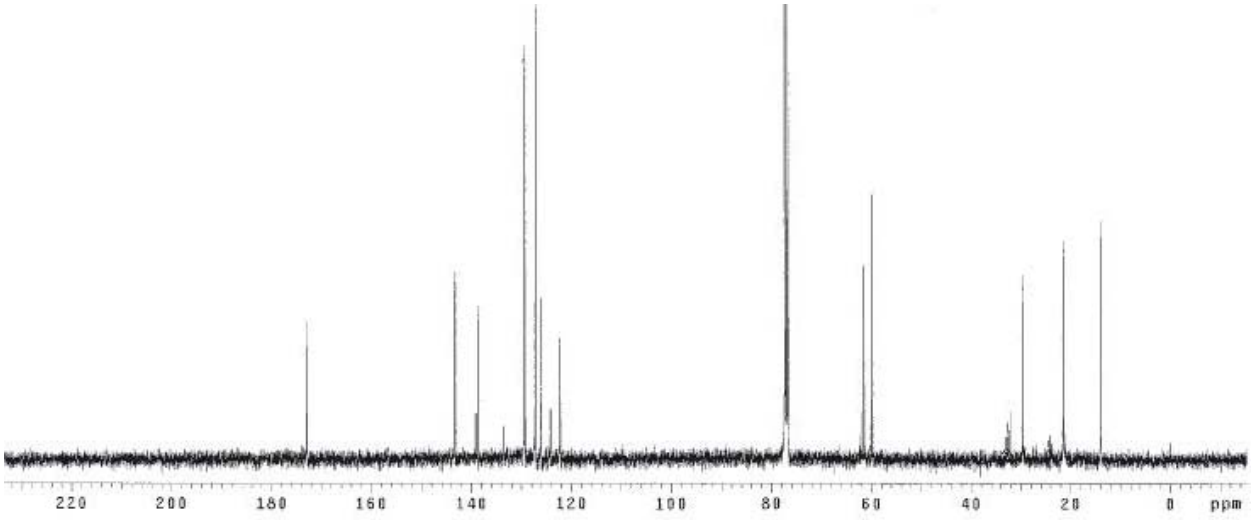
HRMS (CI):Calcd. for $C_{16}H_{19}D_2NO_4S$ 326.1360 [M+1], Found: 326.1364.

FTIR (neat): 3278, 2997, 2921, 2774, 1732, 1449, 1326, 1244, 1159, 1043, 821, 671 cm^{-1}.

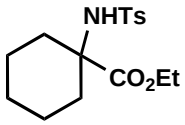
MP: 102-103 ^{o}C (crystals from dichloromethane: hexanes).

R_f : 0.25 in neat dichloromethane.


9
8
7
6
5
4
3
2
1
-0


220
200
180
160
140
120
100
80
60
40
20
0
ppm

Hydrogenation of 15b and *iso*-15b. To an oven dried 10 mL round-bottomed flask equipped with stir bar and charged with **15b** (65 mg, 0.2 mmol, 100 mol%) and Pd/C (21 mg, 10% wt. on carbon, 0.02 mmol, 10 mol%) was added ethyl acetate (3.5 mL, 0.06 M). The reaction vessel was placed under an atmosphere of H_2 (1 atm) and was allowed to stir at room temperature for 24 hours. The solution was filtered through celite with the aid of ethyl acetate (15 mL). The filtrate was concentrated *in vacuo* to furnish a solid, which upon recrystallization (dichloromethane: hexanes) provides ethyl 1-(4-ethylphenylsulfonamido) cyclohexanecarboxylate (60 mg, 0.18 mmol) as colorless crystals in 92% yield.



^{1}H NMR (400MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.86 Hz, 2H), 7.28 (d, *J* = 7.52 Hz, 2H), 5.06 (s, 1H), 3.97 (q, *J* = 7.18 Hz, 2H), 2.42 (s, 3H), 1.84-1.81 (m, 4H), 1.41 – 1.38 (m, 6H), 1.22 (t, *J* = 7.18 Hz, 3H).

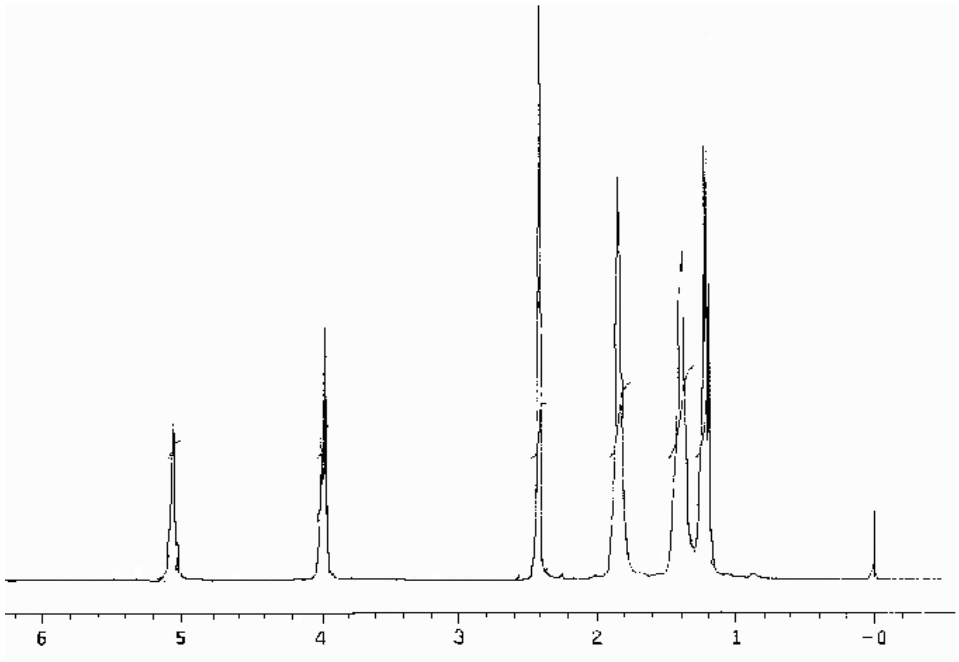
^{13}C NMR (400MHz, $CDCl_3$): δ 173.9, 143.2, 138.6, 129.3, 127.6, 61.4, 61.2, 33.1, 24.9, 21.5, 21.0, 13.9.

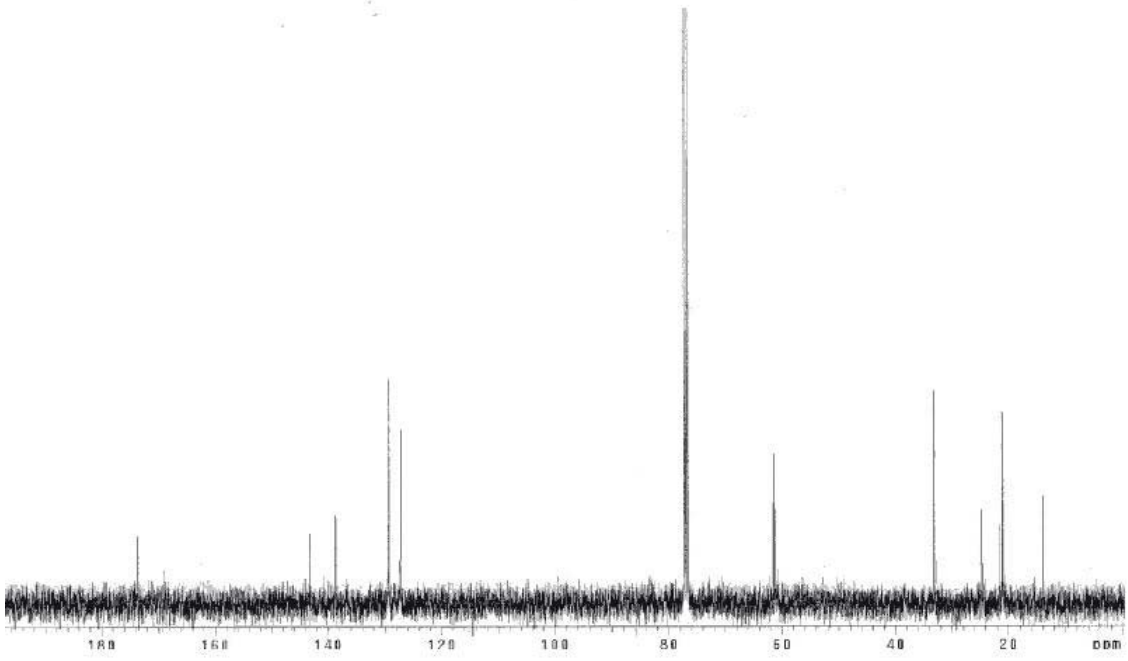
HRMS (CI): Calcd. for $C_{16}H_{23}NO_4S$ 326.1348 [M+1], Found: 326.1351.

FTIR (neat): 3285, 2953, 1733, 1321, 1234, 1092, 1054, 819, 666 cm^{-1}.

MP: 106-107 ^oC (crystals from dichloromethane: hexanes).

R_f : 0.3 in neat dichloromethane.


6
5
4
3
2
1
-0


180
160
140
120
100
80
60
40
20
ppm

DFT Data

Table S1. *Computational details*

All calculations were carried out using Density Functional Theory[1] as implemented in the Jaguar 7.0[2] suite of *ab initio* quantum chemistry programs. Geometries were optimized by using the B3LYP[3, 4] functional with the 6-31G** basis set. Rhodium was represented by the Los Alamos LACVP basis,[5, 6] which includes relativistic effective core potentials. The energies were reevaluated by additional single point calculations at each optimized geometry using Dunning's correlation consistent triple-ζ basis set cc-pVTZ(-f)[7] with the standard double set of polarization functions. In these single-point calculations, Rh was described by a modified version of LACVP, designated as LACV3P, where the exponents were decontracted to match the effective core potential with the triple-ζ quality basis. Vibrational frequency calculation results based on analytical second derivatives at the B3LYP/6-31G**/LACVP level of theory were used to confirm proper convergence to local minima and maxima for equilibrium and transition state geometries, respectively, and to derive the zero-point-energy (ZPE) and vibrational entropy corrections at room temperature. Unscaled vibrational frequencies are used for these corrections. Solvation energies were evaluated by a self-consistent reaction field (SCRF)[8-10] approach, based on accurate numerical solutions of the Poisson-Boltzmann equation.[8, 11] In the results reported below, solvation calculations were carried out at the gas-phase geometry using the 6-31G**/LACVP basis and employing a dielectric constant of ε = 10.3 for DCE.

References

1. Parr, R. G.; Yang, W., *Density Functional Theory of Atoms and Molecules*. Oxford University Press: New York, 1989.
2. Jaguar 7.0, Schrödinger, Inc., Portland, Oregon, 2003.
3. Becke, A. D., *J. Chem. Phys.* **1993,** *98*, 5648-5652.
4. Lee, C. T.; Yang, W. T.; Parr, R. G., *Phys. Rev. B* **1988,** *37*, 785-789.
5. Hay, P. J.; Wadt, W. R., *J. Chem. Phys.* **1985,** *82*, 270-283.
6. Hay, P. J.; Wadt, W. R., *J. Chem. Phys.* **1985,** *82*, 299-310.
7. Dunning, T. H., *J. Chem. Phys.* **1989,** *90*, 1007-1023.
8. Marten, B.; Kim, K.; Cortis, C.; Friesner, R. A.; Murphy, R. B.; Ringnalda, M. N.; Sitkoff, D.; Honig, B., *J. Phys. Chem.* **1996,** *100*, 11775-11788.
9. Friedrichs, M.; Zhou, R. H.; Edinger, S. R.; Friesner, R. A., *J. Phys. Chem. B* **1999,** *103*, 3057-3061.
10. Edinger, S. R.; Cortis, C.; Shenkin, P. S.; Friesner, R. A., *J. Phys. Chem. B* **1997,** *101*, 1190-1197.
11. Tannor, D. J.; Marten, B.; Murphy, R. B.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M. N.; Goddard, W. A., III; Honig, B., *J. Am. Chem. Soc.* **1994,** *116*, 11875-11882.

***Table S2**. Optimized structures of all intermediates and transition states for Cycle A, defined according to Figure 2 in the main text.*

==========

3 - Rh(I)BIPHEP bis-acetylene complex

==========

Rh	0.477709699	-0.013730415	-0.339451285
P	-0.355312036	0.247597931	1.845916852
C	-1.764970671	1.443970079	1.985914131
C	-1.556691808	2.704627459	2.568650964
H	-0.585464291	2.959813293	2.972160112
C	-2.582001222	3.643674923	2.668112130
H	-2.384194772	4.607840224	3.127113405
C	-3.850551195	3.332938632	2.189306531
H	-4.660982714	4.052397173	2.259839762
C	-4.078452729	2.080413124	1.625576520
H	-5.068483811	1.829178062	1.257200155
C	-3.059906068	1.121245381	1.507456206
C	-3.037927538	-0.762371168	-0.266828299
C	-3.482267524	-0.208970896	0.958568185
C	-4.477287833	-0.886942260	1.681958851
H	-4.815894698	-0.456254061	2.619467093
C	-5.031345485	-2.084622408	1.234483710
H	-5.794463899	-2.583857999	1.823891373
C	-4.606989352	-2.617645850	0.020664798
H	-5.038559621	-3.537383986	-0.362429389
C	-3.625742373	-1.956183917	-0.718634205
H	-3.329850864	-2.376393727	-1.671200519
P	-1.709344011	0.061171236	-1.266612019
C	2.256981725	-1.163180045	0.449527284
C	2.700552685	-0.021041483	0.346950161
C	1.383338444	0.799249668	-2.299905308
C	1.448506846	-0.410003273	-2.485699625
H	2.137273735	-2.208685323	0.646064694
H	3.291792960	0.868806706	0.329288729
H	1.433769004	1.864726301	-2.382088574
H	1.573011790	-1.420640402	-2.806409781
C	-2.395815644	1.714578073	-1.676964591
C	-1.584490238	2.854697986	-1.598590505
H	-0.561255244	2.759474201	-1.249326980
C	-2.090525933	4.111871412	-1.934801911
H	-1.451384860	4.987086569	-1.863701770
C	-3.414836744	4.243867003	-2.353262634
H	-3.809612863	5.220917754	-2.614967734
C	-4.234528629	3.114038854	-2.427761377
H	-5.268216802	3.211137703	-2.746541011
C	-3.732078406	1.858333576	-2.089196450
H	-4.382210409	0.989475153	-2.141885654
C	-1.701373596	-0.875667905	-2.854610272
C	-2.141130838	-0.322350254	-4.064680785
H	-2.526979835	0.690172936	-4.096821991
C	-2.083068859	-1.067310859	-5.246276481
H	-2.425834836	-0.620953964	-6.175038029
C	-1.590949400	-2.371646009	-5.237007659
H	-1.552038721	-2.948550110	-6.155815749
C	-1.144749058	-2.930998312	-4.035843677
H	-0.759320095	-3.946344074	-4.016762338
C	-1.191039271	-2.186831221	-2.858259224
H	-0.830766804	-2.628805648	-1.932245835
C	-0.946243709	-1.246298430	2.734980149
C	-1.612298839	-1.129096094	3.968018294
H	-1.805110520	-0.147607396	4.391933002
C	-2.036285135	-2.268173386	4.650562634
H	-2.548307479	-2.164766627	5.602934566
C	-1.808212337	-3.537269844	4.110832987
H	-2.142466059	-4.422954041	4.642786879
C	-1.156606286	-3.661126276	2.883410410
H	-0.986132698	-4.644137678	2.454129556
C	-0.727394910	-2.522045689	2.199273568
H	-0.240125066	-2.620200322	1.233505718
C	0.963581314	0.966951493	2.919777779
C	1.650710400	2.110463456	2.470772594
H	1.393650832	2.552659155	1.511295163
C	2.654809416	2.689894698	3.244429561
H	3.164507689	3.580399376	2.887530473
C	3.005688124	2.126060047	4.474496073
H	3.790871441	2.573662974	5.076097685
C	2.344234633	0.982782885	4.919406230
H	2.613622029	0.532716747	5.870389619
C	1.329368071	0.405419035	4.150504045
H	0.829116818	-0.483061875	4.518199688

==========

3-TS - Oxidative addition TS

==========

Rh	0.428403840	-0.068145613	-0.337784417
P	-0.404960498	0.206951384	1.807663829
C	-1.764015879	1.449684371	1.941629685
C	-1.495717322	2.713699845	2.487865116
H	-0.498235564	2.948700800	2.839793002
C	-2.495879816	3.677988562	2.607383175
H	-2.260112380	4.647310925	3.036356511
C	-3.789758840	3.385719424	2.186454324
H	-4.579836161	4.125168448	2.277195242
C	-4.071049575	2.131426774	1.649272909
H	-5.079286767	1.901722750	1.317958991
C	-3.079449373	1.149563350	1.507407880
C	-3.026403075	-0.756507070	-0.229774503
C	-3.516835611	-0.176836970	0.966425362
C	-4.533604018	-0.843547392	1.667052115
H	-4.910985168	-0.396573908	2.581839958
C	-5.053523709	-2.059701178	1.227533556
H	-5.836476248	-2.552304771	1.795982589
C	-4.564130657	-2.628383644	0.054873911
H	-4.961507139	-3.571042342	-0.309475590
C	-3.563208936	-1.977215701	-0.666392101
H	-3.209939252	-2.422899041	-1.588752547
P	-1.712439552	0.078863496	-1.225787366
C	2.640304027	-0.761461134	-0.238489204
C	1.846459268	-1.334805718	0.573043081
C	1.034858051	0.902828796	-2.109635392
C	1.996866229	0.074087390	-2.043229025
H	3.669821839	-0.504492456	-0.417864072
H	1.847757615	-1.916754894	1.479309772
H	0.534997026	1.557080943	-2.803755918
H	2.750164797	-0.438773189	-2.615648028
C	-2.445541630	1.716892220	-1.621073685
C	-1.695362778	2.894278425	-1.499022416
H	-0.676147553	2.846442210	-1.129125193
C	-2.259801468	4.129005561	-1.827193656
H	-1.668089839	5.034006264	-1.724591651

C	-3.577638876	4.201398582	-2.278945376
H	-4.014412724	5.161623395	-2.536653427
C	-4.337579939	3.033685135	-2.390066588
H	-5.367077460	3.083197390	-2.732761543
C	-3.780160083	1.799858967	-2.058092433
H	-4.386232604	0.901472366	-2.135573145
C	-1.637855507	-0.845631427	-2.814647864
C	-2.165513982	-0.347895358	-4.014516905
H	-2.669468221	0.611636869	-4.038078235
C	-2.040350864	-1.082181452	-5.196362281
H	-2.451044673	-0.683298729	-6.119246053
C	-1.393046645	-2.316597951	-5.194562306
H	-1.299227525	-2.884660682	-6.115361328
C	-0.859320298	-2.818370449	-4.004625822
H	-0.349532655	-3.777445817	-3.995990914
C	-0.972016564	-2.085310838	-2.825731134
H	-0.535091457	-2.472038386	-1.909031921
C	-1.043455432	-1.233811960	2.748210326
C	-1.675833809	-1.034213030	3.988696589
H	-1.809521447	-0.028860348	4.378028504
C	-2.143089892	-2.122262561	4.723053623
H	-2.625775728	-1.957226966	5.681972495
C	-1.995643594	-3.419288183	4.225093761
H	-2.363250860	-4.265776094	4.797765455
C	-1.384531190	-3.624050372	2.988488945
H	-1.279910685	-4.629673351	2.591849078
C	-0.910616021	-2.536998826	2.251724266
H	-0.454771417	-2.698309323	1.280116039
C	0.984060174	0.887294297	2.804378538
C	1.771789454	1.904622358	2.234904354
H	1.546860816	2.265753863	1.235035086
C	2.844204432	2.447807577	2.938603717
H	3.438263039	3.238486459	2.489637579
C	3.158224209	1.970891260	4.213852980
H	3.997776655	2.389971866	4.760487519
C	2.394380424	0.950957578	4.778774581
H	2.637880333	0.570144037	5.766250311
C	1.311470437	0.410209291	4.081679129
H	0.732474528	-0.384673548	4.537721652

==========

4 - Rh-(III)-BIPHEP Rhodacyclopentadiene

==========

Rh	0.235394163	0.223534048	-0.435484490
P	-0.294392752	-0.021347819	1.985875603
C	-1.418004149	1.399238290	2.326677717
C	-0.927114880	2.496170338	3.051013751
H	0.040944809	2.425789597	3.535773805
C	-1.655020694	3.682000174	3.156713488
H	-1.251281818	4.513483393	3.726889421
C	-2.891925563	3.789942315	2.527989357
H	-3.465727531	4.709787192	2.590937417
C	-3.404504835	2.698226826	1.828679522
H	-4.384145348	2.771160300	1.365182676
C	-2.693124607	1.493942128	1.711295461
C	-3.169639722	-0.303304906	-0.135348071
C	-3.437810089	0.339604959	1.099571073
C	-4.562344699	-0.079801567	1.832766845
H	-4.772241843	0.416088141	2.775418584
C	-5.400069202	-1.102847820	1.396277263
H	-6.256809043	-1.395814900	1.995482769
C	-5.127747544	-1.736377436	0.187464131
H	-5.767802895	-2.532931964	-0.179457238
C	-4.027353578	-1.334514903	-0.565830041
H	-3.847592778	-1.821725639	-1.515988210
P	-1.842587239	0.227135435	-1.304074806
C	0.520037082	2.205186683	-0.335011087
C	1.421779599	2.616704509	-1.241777803
C	1.766032514	1.658525804	-2.308113116
C	1.082707714	0.496569410	-2.277345531
H	0.037925539	2.789957379	0.442654646
H	1.840453112	3.623190194	-1.217534612
H	2.498583389	1.914342340	-3.073472051
H	1.158127815	-0.290230467	-3.027980677
C	1.180173460	0.208789500	3.064484981
C	2.280076943	0.930367081	2.567862525
H	2.239882811	1.374024784	1.575547368
C	3.421766452	1.106720351	3.351010251
H	4.263971445	1.666743911	2.954940640
C	3.482581408	0.560526469	4.634342471
H	4.372819904	0.693552230	5.241945256
C	2.396204522	-0.161853831	5.132904520
H	2.439049959	-0.592477580	6.129122586
C	1.252357431	-0.340020773	4.355045999
H	0.421263012	-0.913385474	4.752609521
C	-1.091764886	-1.532746528	2.644080195
C	-2.012810111	-1.496300803	3.701316159
H	-2.307172323	-0.543989650	4.132987205
C	-2.555103789	-2.680300986	4.202243929
H	-3.268155172	-2.642131206	5.020922601
C	-2.181130243	-3.909775172	3.656926929
H	-2.605013826	-4.829715758	4.048955943
C	-1.260990640	-3.955554899	2.608083768
H	-0.963539301	-4.910822087	2.185189475
C	-0.720557804	-2.773215664	2.102584759
H	0.005561198	-2.818871932	1.293492217
C	-1.736650640	-1.122614805	-2.535750437
C	-2.013015880	-0.929496019	-3.895303795
H	-2.356432036	0.035447808	-4.253150137
C	-1.847054410	-1.984046752	-4.795820775
H	-2.069364121	-1.829976273	-5.847645446
C	-1.402491349	-3.229197820	-4.350835778
H	-1.276636485	-4.045350561	-5.056206078
C	-1.125933422	-3.429068031	-2.995519510
H	-0.787704169	-4.399531249	-2.644043382
C	-1.291486780	-2.382502591	-2.091203370
H	-1.105006461	-2.554951651	-1.033036121
C	-2.499717578	1.717186364	-2.132323587
C	-3.860778813	2.052136630	-2.016265275
H	-4.523658746	1.458110036	-1.396370960
C	-4.372839207	3.150086036	-2.708241674
H	-5.425972971	3.398066990	-2.612676484
C	-3.540738544	3.920172821	-3.522585005
H	-3.942622116	4.773422916	-4.060947314
C	-2.190377628	3.585790370	-3.645298949
H	-1.536992537	4.178900802	-4.278382101
C	-1.667212592	2.495624036	-2.952084139
H	-0.618030774	2.242150185	-3.050377446

==========

5 – Rhodacyclopentadiene, aldehyde adduct

==========

Rh	0.338371100	0.119919603	-0.114528988
P	-0.754789443	0.086497521	2.147905717

C	-2.045275571	1.406615030	2.148662209
C	-1.831301489	2.597749227	2.859195553
H	-0.970851631	2.683360277	3.513253251
C	-2.706764746	3.679232231	2.750247358
H	-2.512528476	4.587072820	3.313951235
C	-3.823153660	3.583903227	1.924735883
H	-4.511488144	4.417810679	1.826192389
C	-4.062887191	2.396160705	1.234216298
H	-4.948783067	2.309213635	0.612279727
C	-3.191618359	1.299057057	1.319743502
C	-3.047024678	-0.594795270	-0.473867556
C	-3.638784050	0.025560725	0.656419733
C	-4.802555306	-0.547963351	1.196656216
H	-5.261997533	-0.062946173	2.052056121
C	-5.370825963	-1.710055799	0.679613082
H	-6.268400019	-2.121849243	1.130968986
C	-4.778955304	-2.326149048	-0.418848909
H	-5.204640989	-3.228838501	-0.846037627
C	-3.637294061	-1.764186327	-0.988858961
H	-3.210866728	-2.239696958	-1.862852714
P	-1.588808775	0.116143147	-1.371348496
C	0.514741707	2.119145940	-0.099714629
C	1.415362465	2.601319818	-0.975097345
C	1.955813540	1.638813260	-1.939302323
C	1.461221681	0.389298282	-1.828922992
H	-0.080531280	2.696397096	0.603195149
H	1.679777905	3.659250434	-0.996655441
H	2.668263805	1.946414732	-2.705127859
H	1.720752175	-0.427486727	-2.502697886
C	4.048904251	0.717286393	0.934155050
C	3.340140741	-0.588768599	1.021066859
H	4.891699388	0.615092053	0.238165523
H	3.386169808	1.518682078	0.610507120
H	4.485359121	0.945362643	1.915088360
H	3.943296989	-1.461758773	1.328219471
O	2.150740210	-0.783107464	0.787916897
C	-2.246720273	1.594383362	-2.228535948
C	-1.366099148	2.442109636	-2.920128936
H	-0.304795257	2.230715756	-2.918554978
C	-1.856580250	3.539954230	-3.624836505
H	-1.165776618	4.186717617	-4.157929377
C	-3.226668666	3.806596164	-3.647526232
H	-3.605564164	4.665567310	-4.193831232
C	-4.108211339	2.962380594	-2.972176160
H	-5.176549097	3.157009455	-2.995265534
C	-3.624823311	1.859349050	-2.268230891
H	-4.323958282	1.204585117	-1.760234012
C	-1.230185411	-1.112579589	-2.693812266
C	-1.491587594	-0.863586667	-4.047094368
H	-1.950184368	0.070642144	-4.352308601
C	-1.161046620	-1.817882723	-5.013196247
H	-1.370156031	-1.612844873	-6.059079239
C	-0.569049889	-3.025033743	-4.641686168
H	-0.315601957	-3.763937371	-5.395898491
C	-0.306308591	-3.281822985	-3.292551279
H	0.150277215	-4.221146302	-2.994160020
C	-0.631850918	-2.331979784	-2.326554338
H	-0.436689809	-2.550617885	-1.278185095
C	0.437908921	0.541904522	3.487439159
C	1.403640972	1.536877537	3.245957726
H	1.426553061	2.051080940	2.290330702
C	2.334713879	1.881259147	4.226252436
H	3.061508042	2.663817359	4.024586948
C	2.334801605	1.225377095	5.459516948
H	3.062859037	1.489676895	6.220770907
C	1.390011154	0.229191809	5.705199660
H	1.380304452	-0.289577467	6.659531928
C	0.448305812	-0.110095904	4.730919697
H	-0.276225673	-0.887127244	4.946685243
C	-1.559892271	-1.435076821	2.784833140
C	-2.593447525	-1.394016564	3.734061512
H	-2.972496900	-0.437105352	4.081874533
C	-3.136566883	-2.576701901	4.235737219
H	-3.934320584	-2.532442392	4.971789096
C	-2.656275554	-3.813301864	3.797084118
H	-3.081252467	-4.732358080	4.189273149
C	-1.630586536	-3.863082058	2.851671204
H	-1.253271604	-4.821626901	2.507021169
C	-1.086040567	-2.680855732	2.346656151
H	-0.279573823	-2.727911476	1.618505697

==========

5-TS - Aldehyde insertion TS

==========

C	-1.615075132	3.350741157	1.197628627
C	-2.509166955	3.154592590	2.261948507
H	-2.174293870	3.379065710	3.270504150
C	-3.810423832	2.697306310	2.057805363
H	-4.471722414	2.548515610	2.906162244
C	-4.255130386	2.456274552	0.761914492
H	-5.272532701	2.123460272	0.579058740
C	-3.384844619	2.644274589	-0.312146377
H	-3.741585242	2.450441832	-1.317445399
C	-2.062880057	3.076038426	-0.119772797
P	-0.903384670	3.029756932	-1.551191565
C	-0.315607375	4.022999962	1.540296432
C	-0.457199568	5.321608810	2.063212268
H	-1.456797993	5.739577916	2.134061560
C	0.632615553	6.079601363	2.478457614
H	0.478443645	7.080470161	2.870782035
C	1.912849000	5.541483038	2.388167738
H	2.778860315	6.111770519	2.709994539
C	2.080170062	4.253694589	1.887881377
H	3.081464711	3.842570220	1.844144705
C	0.988196318	3.476298562	1.456208327
P	1.367004142	1.748169084	0.919009597
Rh	0.586718756	1.095216015	-1.178904374
C	-0.810852093	-0.055174438	-0.422555220
C	-0.515894035	-1.382020876	-0.304967177
H	-1.776429686	0.374211734	-0.161406122
H	-1.256878162	-2.103637249	0.035420599
C	0.824536836	-1.755436906	-0.641025325
C	1.608097832	-0.762789472	-1.186493135
H	1.190069881	-2.765133127	-0.446254469
H	2.684274004	-0.886756566	-1.296417545
O	0.756590547	0.718843144	-3.191765939
C	1.073902056	-0.538195401	-3.197735293
C	2.304086613	-0.971958039	-3.949741940
H	0.246595262	-1.256111118	-3.162961369
H	2.565536886	-2.008237032	-3.722529534
H	2.085882389	-0.900730130	-5.024096184
H	3.150363209	-0.314784747	-3.734856754
C	-1.966492116	2.792465720	-3.034929652
C	-2.465793078	3.886485338	-3.760351784

H	-2.220317617	4.899766378	-3.461271246
C	-3.275798433	3.681817358	-4.877191211
H	-3.652829794	4.537155620	-5.430248915
C	-3.597999121	2.386489955	-5.283875003
H	-4.226304962	2.229577132	-6.155870964
C	-3.107127357	1.292732216	-4.569105311
H	-3.352254341	0.282059280	-4.882842529
C	-2.292137751	1.491792552	-3.455358341
H	-1.908600712	0.634037538	-2.914011135
C	-0.222223545	4.715762586	-1.796540156
C	0.923814802	4.854878867	-2.597205314
H	1.401297027	3.974019055	-3.021016004
C	1.434890157	6.120679621	-2.886158562
H	2.317186804	6.215783742	-3.512492948
C	0.809973798	7.261999874	-2.378646216
H	1.207312590	8.247121888	-2.604068467
C	-0.333004584	7.131685525	-1.587559556
H	-0.829154445	8.015968111	-1.197660534
C	-0.849968101	5.867141133	-1.299298625
H	-1.746587776	5.778450188	-0.693496589
C	3.159584645	1.810230913	0.503452937
C	3.518163161	2.530074833	-0.652919965
H	2.765552551	3.090437339	-1.203472579
C	4.844970008	2.573023575	-1.077962540
H	5.107718675	3.138026210	-1.967664965
C	5.833920534	1.902869077	-0.352930754
H	6.868661303	1.939137623	-0.679811771
C	5.487110357	1.198976658	0.801309927
H	6.253557082	0.688487411	1.377097102
C	4.157943181	1.148665451	1.230623096
H	3.907622849	0.601769477	2.133208453
C	1.181959813	0.734638027	2.437506641
C	0.642483394	1.283970812	3.611272085
H	0.341916221	2.324924576	3.640546036
C	0.500802053	0.500165087	4.757373532
H	0.083890838	0.941402179	5.657883671
C	0.898608309	-0.836532165	4.751344047
H	0.790704487	-1.442834114	5.645582139
C	1.443336615	-1.388938558	3.589887231
H	1.763651364	-2.426704607	3.577985124
C	1.581022791	-0.614060062	2.439577411
H	2.007065027	-1.055352524	1.546902193

==========

6 - Aldehyde insertion product - Rhodacycloheptadiene

==========

C	-2.161946888	3.360177916	0.864654919
C	-3.026769579	3.642350449	1.935504067
H	-2.811170536	4.505039652	2.558110844
C	-4.136572161	2.851845780	2.224696635
H	-4.774581759	3.103867301	3.066563263
C	-4.418850492	1.747145741	1.428175785
H	-5.282467764	1.121708335	1.632170341
C	-3.587619058	1.448450343	0.351335875
H	-3.826250103	0.595374832	-0.272736479
C	-2.459294249	2.233188070	0.049906744
P	-1.427012270	1.655820426	-1.355041243
C	-1.055518978	4.355266646	0.658121413
C	-1.450095808	5.684694345	0.433541541
H	-2.510167626	5.905869048	0.347967446
C	-0.522663759	6.716967640	0.312888483
H	-0.864261961	7.731589102	0.130416271
C	0.836072562	6.440289037	0.436564657
H	1.571728953	7.234648492	0.354726243
C	1.251922015	5.133517584	0.684672082
H	2.309904430	4.931995960	0.807145845
C	0.327659452	4.083462208	0.797226859
P	0.913151689	2.376637415	1.150379658
Rh	0.557743890	0.858500502	-0.643635484
C	-0.233467736	-0.554004119	0.475075766
C	0.264938500	-1.801694105	0.454556872
H	-1.054653347	-0.278411213	1.133231382
H	-0.176997341	-2.471447964	1.199149805
C	1.357966191	-2.427119643	-0.301994898
C	1.943544925	-2.139804588	-1.480688029
H	1.747541061	-3.310921703	0.201313670
H	2.752388195	-2.809643599	-1.773274644
O	0.595671232	-0.223514846	-2.325776041
C	1.681828856	-1.090712840	-2.534271266
C	2.988448879	-0.333041490	-2.858926307
H	1.416418124	-1.664969468	-3.441992326
H	2.812803775	0.359602607	-3.687700150
H	3.336870944	0.239309019	-1.990562523
H	3.791596479	-1.017868375	-3.150420594
C	2.748629608	2.429503481	1.062293653
C	3.575009073	2.170580696	2.165920215
H	3.139280049	1.983288577	3.141450728
C	4.962644846	2.148313286	2.013832721
H	5.591055270	1.950248473	2.877135693
C	5.543120811	2.385230475	0.766365068
H	6.623131233	2.370015270	0.655832890
C	4.730199193	2.649376763	-0.338522676
H	5.173884950	2.843746587	-1.310429701
C	3.342711739	2.666763856	-0.194582430
H	2.722464518	2.898530958	-1.058335575
C	0.502307289	2.080036744	2.912822937
C	0.146507007	3.139370415	3.762920588
H	0.084394643	4.152123991	3.378242009
C	-0.118457250	2.899704207	5.111031232
H	-0.390287731	3.726859956	5.760358750
C	-0.028321746	1.605365602	5.625147017
H	-0.234300678	1.421737491	6.675647746
C	0.332946351	0.548240688	4.788122021
H	0.410241453	-0.459737757	5.184959375
C	0.595909582	0.780021627	3.438272844
H	0.873439683	-0.048652003	2.795799606
C	-2.447119272	0.479799486	-2.315664499
C	-2.362815309	-0.907274936	-2.128724535
H	-1.633630050	-1.317729039	-1.443103323
C	-3.201743087	-1.756944608	-2.849621076
H	-3.127619200	-2.830482267	-2.703371912
C	-4.119943181	-1.236224041	-3.762011597
H	-4.766911085	-1.903224484	-4.324304473
C	-4.201135273	0.143341580	-3.957748109
H	-4.908884717	0.554848218	-4.671216411
C	-3.367259346	1.000975599	-3.243104334
H	-3.433406127	2.070088324	-3.415016564
C	-1.102308017	3.022289267	-2.516769156
C	-0.093775848	2.830152025	-3.477722488
H	0.471732414	1.901480247	-3.482359109
C	0.140200597	3.810514836	-4.441030477
H	0.918070340	3.659219120	-5.183645601
C	-0.631548876	4.974231166	-4.461498445
H	-0.449208815	5.734101438	-5.215786915

C	-1.648577353	5.155533406	-3.522300124
H	-2.260884414	6.052233391	-3.547864644
C	-1.886289265	4.185200966	-2.549383064
H	-2.686127967	4.328670558	-1.830897771

==========

7 - Rhodacycloheptadiene with acetate, protonated

==========

C	-1.852680811	3.469109966	1.072408214
C	-2.657537246	3.835522559	2.161510399
H	-2.354856715	4.684465836	2.767394631
C	-3.815932489	3.135940574	2.490355054
H	-4.408706946	3.441577627	3.347444583
C	-4.206267851	2.051191717	1.711341649
H	-5.110258959	1.497394294	1.946460668
C	-3.442596621	1.687381532	0.603302038
H	-3.790433378	0.873862231	-0.020985299
C	-2.268348704	2.377626779	0.264783745
P	-1.343410630	1.929631165	-1.269973335
C	-0.672589214	4.340988455	0.767707234
C	-0.954155465	5.698432382	0.534367371
H	-1.984964203	6.030966308	0.608746334
C	0.036740484	6.606891974	0.172711529
H	-0.219324742	7.647011689	-0.005101091
C	1.346062339	6.159140233	0.010751010
H	2.128800034	6.841565165	-0.306598212
C	1.656615682	4.825568140	0.265854254
H	2.678953741	4.493575898	0.136116349
C	0.676496311	3.910068151	0.688092617
P	1.207694493	2.174907063	1.003091979
Rh	0.843645072	1.065418139	-1.020545768
C	0.052931458	-0.549811171	-0.158463903
C	0.372022186	-1.824438867	-0.443349551
H	-0.663878409	-0.381011875	0.643606804
H	-0.089961197	-2.579244888	0.201519539
C	1.294199342	-2.410375400	-1.418458437
C	1.621335219	-2.090796480	-2.681542705
H	1.783470651	-3.309814183	-1.042486717
H	2.349236553	-2.743575537	-3.160876629
O	0.528119897	0.114587541	-2.998236150
C	1.107918051	-1.062243827	-3.646422041
C	2.190830750	-0.630077223	-4.636548584
H	0.272533657	-1.510823309	-4.205151474
O	2.932347874	0.518176361	-1.288844974
C	3.236241206	1.623516686	-1.855417906
O	2.344580203	2.517704260	-1.999734609
C	4.639903802	1.845989530	-2.357053303
H	4.673986631	1.662256342	-3.436872554
H	5.338807985	1.169445746	-1.863581967
H	4.932841067	2.885129416	-2.190202813
H	1.807600325	0.116299255	-5.342969568
H	3.053501132	-0.216163980	-4.108882552
H	2.526276701	-1.489326702	-5.225118053
H	0.416746908	0.794833301	-3.676704688
C	2.963646601	2.224553916	1.573961748
C	3.444834690	3.301577425	2.340415241
H	2.834430722	4.183418030	2.500718775
C	4.715210708	3.250050633	2.912301885
H	5.074075199	4.096202612	3.491263321
C	5.515537021	2.117133933	2.752707269
H	6.504306860	2.079433627	3.200384198
C	5.029165122	1.030089731	2.026875611
H	5.635101255	0.136156651	1.909943836
C	3.760408026	1.075870410	1.445177219
H	3.405310479	0.226320629	0.876637445
C	0.443095033	1.614942647	2.585310213
C	0.043112858	2.551934913	3.550906443
H	0.053881590	3.612073376	3.322810354
C	-0.361986034	2.133776957	4.818175371
H	-0.671845925	2.873575357	5.550836485
C	-0.363288843	0.777488544	5.147387707
H	-0.680645550	0.454145972	6.134338504
C	0.065735857	-0.157640993	4.204738627
H	0.093160357	-1.214089753	4.455939176
C	0.477311696	0.255720907	2.936954139
H	0.837257619	-0.484387726	2.231904405
C	-2.420833692	0.769388051	-2.224144933
C	-2.897791083	1.123190251	-3.497467555
H	-2.663439396	2.091150578	-3.924200270
C	-3.686933596	0.235458621	-4.232514999
H	-4.044698193	0.529562456	-5.215139107
C	-4.019411901	-1.013209895	-3.710318062
H	-4.636821805	-1.698629641	-4.283699494
C	-3.549730524	-1.378428920	-2.446486649
H	-3.796489014	-2.350727253	-2.030301543
C	-2.752848227	-0.500171310	-1.714418141
H	-2.371763683	-0.821698453	-0.754593208
C	-1.388325874	3.470903958	-2.273918630
C	-2.581365503	4.214995120	-2.335117509
H	-3.444223274	3.914401161	-1.747504802
C	-2.667116607	5.340403272	-3.151985588
H	-3.594488191	5.904902219	-3.192765518
C	-1.566466998	5.740495436	-3.916902951
H	-1.635927910	6.618335157	-4.552903407
C	-0.380736069	5.009594767	-3.854410652
H	0.482551004	5.319292901	-4.436547845
C	-0.286589604	3.877345973	-3.039110996
H	0.656132985	3.345967035	-2.975016931

==========

7A - Rhodacycloheptadiene w bidentate acetate, not protonated

==========

C	-1.917154809	3.354692712	0.910746711
C	-2.854578554	3.668758015	1.909787955
H	-2.642734412	4.508251144	2.565750066
C	-4.027653569	2.940368905	2.085830056
H	-4.722052943	3.207973307	2.877078437
C	-4.295257266	1.875123678	1.232232917
H	-5.205734625	1.292323233	1.340522072
C	-3.396397006	1.564104465	0.213116824
H	-3.647149341	0.758515837	-0.464778955
C	-2.202227432	2.280791444	0.026228104
P	-1.071222785	1.837314555	-1.386489819
C	-0.748313519	4.289733373	0.795731803
C	-1.073427156	5.627649961	0.510438356
H	-2.118895857	5.885783924	0.371448297
C	-0.099055008	6.609825745	0.369198136
H	-0.387403415	7.630298557	0.133003535
C	1.241896615	6.264230867	0.509640380
H	2.022295948	7.007926331	0.376309437
C	1.586105905	4.951593720	0.817948108
H	2.633790703	4.696674717	0.913825961
C	0.613278403	3.953052568	0.996666821
P	1.196791388	2.223774946	1.276815650

Rh	1.110438346	1.230819757	-0.893964125
C	0.541768596	-0.570233386	-0.216844188
C	1.103832251	-1.754064973	-0.531503124
H	-0.226345659	-0.575651794	0.558296220
H	0.803008962	-2.619663813	0.069097172
C	2.110088948	-2.026964715	-1.559739009
C	2.133964707	-1.493422711	-2.790533210
H	2.891196914	-2.738902057	-1.288775255
H	2.956212133	-1.743652433	-3.457118671
O	1.156527938	0.761987341	-2.870822821
C	1.059625928	-0.557561767	-3.310782691
C	1.052087477	-0.530389164	-4.847659203
H	0.088425651	-1.007436001	-3.032354461
O	3.272258601	0.986812870	-1.026299683
C	3.442656054	2.157869645	-1.512922368
O	2.482072245	2.980909528	-1.557221813
C	4.803683814	2.528832738	-2.056448773
H	4.893222734	2.134427796	-3.074786204
H	5.594541013	2.080776341	-1.449772398
H	4.917636010	3.614098170	-2.091700639
O	0.974343915	0.451824881	-5.550034820
O	1.117566533	-1.792336458	-5.351431713
C	2.849175129	2.390513996	2.096177003
C	3.053023052	3.335698309	3.117579704
H	2.271383134	4.045556122	3.369705079
C	4.256270522	3.375902314	3.817002874
H	4.401578104	4.120305211	4.595468919
C	5.267629936	2.457236392	3.524432318
H	6.206201202	2.488332269	4.071545167
C	5.063279398	1.499727149	2.533300933
H	5.841687849	0.777371834	2.302944649
C	3.861323685	1.461151710	1.820685000
H	3.723286591	0.732548649	1.031876858
C	0.296114172	1.564779026	2.753386330
C	-0.360642105	2.392218914	3.674758973
H	-0.445943661	3.456612798	3.483023277
C	-0.901198567	1.862910826	4.847257908
H	-1.410657101	2.520764500	5.546558468
C	-0.785181244	0.500023058	5.125029196
H	-1.206861500	0.089571407	6.038284206
C	-0.111070974	-0.327919581	4.226080112
H	0.002318670	-1.387595867	4.438074058
C	0.430222981	0.198795459	3.052727366
H	0.972452713	-0.453048546	2.376222050
C	-2.008432482	0.587279659	-2.369345077
C	-2.437250489	0.878142351	-3.672483062
H	-2.226583406	1.845359486	-4.111724574
C	-3.120814292	-0.078464066	-4.425319184
H	-3.434326980	0.164821163	-5.436692898
C	-3.393599915	-1.336070350	-3.889388464
H	-3.924987214	-2.079191087	-4.477732514
C	-2.968160602	-1.638889760	-2.595036551
H	-3.161341496	-2.620153827	-2.170311049
C	-2.273336867	-0.690583823	-1.845341762
H	-1.922161774	-0.957453920	-0.856197649
C	-1.097593687	3.321298193	-2.470839674
C	-2.177859555	4.218784874	-2.441253280
H	-2.990233321	4.074570318	-1.735335175
C	-2.219573083	5.297127220	-3.323480114
H	-3.059888311	5.985918657	-3.293438062
C	-1.186168523	5.487322354	-4.243856787
H	-1.219139462	6.328270940	-4.931996432
C	-0.119006285	4.590623481	-4.284338409
H	0.680817506	4.724735710	-5.006956873
C	-0.067527149	3.506037129	-3.406878413
H	0.743245311	2.788544238	-3.463701037
C	1.104286029	-1.879015491	-6.782089818
H	1.183925774	-2.941574109	-7.016894669
H	0.176620373	-1.466805376	-7.189626703
H	1.945696893	-1.329108954	-7.213367255

==========

7A' - Rhodacycloheptadiene with acetate and H2 coordinated

==========

C	-2.363869594	2.151468970	-0.403097199
P	-1.084770631	1.431543884	-1.545531594
C	-1.039379784	4.340908874	0.119032090
P	0.914182012	2.538395094	1.249804301
Rh	1.002748691	0.940058973	-0.563389901
C	0.200477737	-0.559152868	0.498617781
C	0.633958587	-1.831051184	0.574190947
H	-0.645536544	-0.278308937	1.128522890
H	0.143512986	-2.466441515	1.320757279
C	1.702542648	-2.488078582	-0.183651705
C	1.946597167	-2.343831807	-1.494704307
H	2.329634595	-3.175351190	0.385934415
H	2.784259938	-2.876511437	-1.938603476
O	1.281079833	-0.109789448	-2.287479027
C	1.089912378	-1.483548866	-2.402413003
C	1.272746908	-1.839454301	-3.886551530
H	0.041943401	-1.770267715	-2.193431076
O	1.265069005	-1.059532921	-4.811739373
O	1.388949999	-3.182763432	-4.057659933
C	2.564077522	2.977323574	1.966580178
C	2.736130030	3.182374768	3.344197548
H	1.901801376	3.064208548	4.025519402
C	3.983512584	3.539842755	3.858963331
H	4.096363275	3.689605517	4.929401155
C	5.075602109	3.703576338	3.008217202
H	6.046518810	3.979638824	3.410827944
C	4.913708876	3.505129047	1.636288785
H	5.756295649	3.619588422	0.960188909
C	3.671283492	3.142021765	1.118015004
H	3.587399094	2.968391071	0.052006262
C	-0.056040070	2.197739058	2.776555465
C	-0.827589820	3.177785912	3.416437534
H	-0.917748332	4.166834050	2.979749338
C	-1.465782808	2.898358031	4.625237745
H	-2.060528700	3.667997266	5.109675953
C	-1.334045821	1.640196349	5.213971756
H	-1.831451093	1.423744310	6.155496982
C	-0.550852857	0.664904651	4.595013749
H	-0.430471278	-0.312383793	5.054304841
C	0.088519724	0.940184157	3.386046172
H	0.707951360	0.180973687	2.920018109
C	-1.974049682	0.012785453	-2.338080972
C	-2.424838074	0.098994744	-3.663949486
H	-2.225126810	0.985908104	-4.252205975
C	-3.126554666	-0.956941923	-4.248288924
H	-3.457873785	-0.869746323	-5.279273625
C	-3.397589752	-2.113873612	-3.519664586
H	-3.943882562	-2.934438827	-3.976740250
C	-2.955178646	-2.212633879	-2.200231872
H	-3.149102858	-3.112290330	-1.622704183

C	-2.244951126	-1.163688582	-1.616734967
H	-1.885236347	-1.271247482	-0.601276417
C	-0.916502618	2.605635668	-2.949542588
C	-1.842819023	3.629426587	-3.191203563
H	-2.682325471	3.776110004	-2.519313849
C	-1.698472374	4.458977080	-4.303895062
H	-2.417729363	5.254575588	-4.479465168
C	-0.636926575	4.264305418	-5.188149300
H	-0.525523324	4.911545950	-6.054191333
C	0.272815053	3.228330954	-4.965836706
H	1.089542375	3.058077891	-5.661407687
C	0.140092151	2.395909147	-3.854029732
H	0.824486590	1.563493743	-3.701960356
C	-3.555116432	1.437644239	-0.181564036
C	-2.176720479	3.374169962	0.291675552
O	4.056300979	1.338576080	-1.482561202
O	2.877810735	0.291795285	0.142795713
C	3.939877994	0.506700351	-0.567431089
C	5.130276673	-0.351907655	-0.154076343
H	4.867338221	-1.408753416	-0.259245688
H	5.998334543	-0.119689649	-0.773448186
H	5.367810408	-0.175322448	0.899893627
H	1.695923635	2.518888899	-1.581882962
H	2.376098185	2.124545163	-1.603147862
H	-3.729411834	0.512917829	-0.714926067
C	-4.538727789	1.887878372	0.695420176
C	-4.360481215	3.091324037	1.367740500
C	-3.196262991	3.820701518	1.151156591
C	-1.396221739	5.582116422	-0.438117486
C	-0.488397657	6.628799379	-0.566750790
C	0.811883699	6.452915412	-0.104623569
C	1.183624868	5.238937358	0.469338027
C	0.286609387	4.162789530	0.588632879
H	-5.441245301	1.300332704	0.837786177
H	-5.118194056	3.466011649	2.050085465
H	-3.057822769	4.768901182	1.662169621
H	-2.418735810	5.717496597	-0.777797331
H	-0.799361052	7.568078824	-1.014752047
H	1.540700804	7.254789154	-0.181087288
H	2.196455905	5.131319713	0.835292704
C	1.507947420	-3.613218624	-5.420214236
H	1.602597407	-4.699429965	-5.381904083
H	0.623688146	-3.326926455	-5.997062063
H	2.388684513	-3.169347645	-5.892643588

==========

7A'-TS - H2 activation TS

==========

C	-2.453079430	2.123326385	-0.515094437
P	-1.072781945	1.739428594	-1.683065188
C	-1.351028837	4.325259693	0.309694133
P	0.895607004	2.672079487	1.000725728
Rh	0.788754631	0.926222506	-0.528344037
C	-0.466118916	-0.237194325	0.622955636
C	-0.325828914	-1.541001864	0.941768186
H	-1.327075051	0.260796531	1.070341321
H	-1.051409838	-1.951078448	1.652588298
C	0.734883573	-2.494229800	0.592973971
C	1.299871214	-2.751888514	-0.597507845
H	1.085062978	-3.099494932	1.431171943
H	2.084561629	-3.501344850	-0.653631661
O	1.079773223	-0.709615059	-1.987586656
C	0.869532613	-2.132489190	-1.899531505
C	1.609513621	-2.698233170	-3.113863412
H	-0.201810733	-2.302253058	-2.052356964
O	2.214215512	-1.968389842	-3.880753275
O	1.511549076	-4.015322285	-3.225628959
C	2.665041088	3.165433600	1.200462444
C	3.282690659	3.161749732	2.460556770
H	2.735594817	2.837311236	3.337955060
C	4.607795811	3.582180484	2.600139136
H	5.068817790	3.571668790	3.583454401
C	5.332178222	4.019067886	1.491533954
H	6.360727276	4.348374358	1.604329648
C	4.722824616	4.034017796	0.234405015
H	5.274894050	4.373587032	-0.636990585
C	3.404343566	3.607328542	0.088622884
H	2.946584889	3.628741373	-0.893764704
C	0.353633006	2.256711483	2.701482319
C	-0.382346663	3.159982931	3.481413667
H	-0.687196121	4.116490204	3.071443052
C	-0.714176706	2.839977214	4.798268478
H	-1.285453713	3.545381088	5.394411960
C	-0.306952388	1.624784437	5.348285509
H	-0.563617487	1.379567497	6.374746571
C	0.438414200	0.727379892	4.580434289
H	0.765329087	-0.216074996	5.008033307
C	0.766952694	1.035239430	3.261992767
H	1.348367109	0.338054250	2.668744824
C	-1.711134498	0.481091034	-2.868480275
C	-1.760333606	0.755665717	-4.243484903
H	-1.430386102	1.714899609	-4.624792517
C	-2.234960037	-0.202603470	-5.141140278
H	-2.261921228	0.028468080	-6.201949668
C	-2.676873562	-1.441688377	-4.681628223
H	-3.055108831	-2.181093659	-5.381375431
C	-2.626944774	-1.728007374	-3.315298445
H	-2.965398528	-2.692068908	-2.945705691
C	-2.135271178	-0.781947295	-2.417079686
H	-2.069176102	-1.032149728	-1.363303326
C	-0.907224230	3.241282338	-2.729579088
C	-2.070175623	3.945413547	-3.088537308
H	-3.034769226	3.643272372	-2.690978215
C	-1.996189882	5.029654557	-3.960119122
H	-2.901641389	5.565127311	-4.230474369
C	-0.763602334	5.424023426	-4.486116174
H	-0.707177738	6.270117873	-5.164854582
C	0.393124683	4.727064209	-4.139777654
H	1.353326172	5.025643073	-4.550322919
C	0.323195208	3.638932855	-3.267132076
H	1.224762943	3.096177430	-3.008298558
C	-3.585960313	1.297348989	-0.453049695
C	-2.351273306	3.207949238	0.393940074
H	1.669673128	-0.555376253	-2.751358858
O	3.824901179	0.660678267	-1.158779034
O	2.478887567	0.116725779	0.552941554
C	3.608864838	0.114396769	-0.021985371
C	4.768670011	-0.549081610	0.677114612
H	4.465474847	-1.533393219	1.042455520
H	5.623817095	-0.636613488	0.007306584
H	5.047764225	0.056397014	1.545653557
H	1.865428328	1.831306743	-1.590430957
H	2.761161191	1.287290395	-1.456684887
H	-3.710349683	0.497762163	-1.170734159
C	-4.579880595	1.486236099	0.505908366

C	-4.458090111	2.517900414	1.430064877
C	-3.363085566	3.373970995	1.354073624
C	-1.911385464	5.584054805	0.025074800
C	-1.145835040	6.745586271	-0.025088795
C	0.219412533	6.667945531	0.232356266
C	0.797142951	5.434775020	0.525437624
C	0.040382256	4.249516327	0.562105347
H	-5.442165347	0.826541829	0.521783648
H	-5.216565956	2.673112259	2.191315125
H	-3.287895818	4.207661854	2.045413135
H	-2.977960017	5.638022499	-0.169166735
H	-1.615844658	7.696846319	-0.255269876
H	0.839479934	7.559061928	0.214534905
H	1.856911624	5.403009562	0.741779562
C	2.192310892	-4.609234454	-4.359994637
H	2.007501493	-5.678801401	-4.278441658
H	1.784418707	-4.212474014	-5.291593257
H	3.261244314	-4.393037514	-4.310269146

==========

8 - Protonated Rhodacycloheptadienehydride, acetic acid adduct (H_2 activation product)

==========

C	-1.890818428	3.865073863	0.756646400
C	-2.565590339	4.640233277	1.711420516
H	-2.294171048	5.687088552	1.812117236
C	-3.546803261	4.099562653	2.538204344
H	-4.042108606	4.727244247	3.273022927
C	-3.880258341	2.754705184	2.412783403
H	-4.642246322	2.311390855	3.046292279
C	-3.241474511	1.972592158	1.450913211
H	-3.539588006	0.937351787	1.349531580
C	-2.248336104	2.499805535	0.606919280
P	-1.534684881	1.404893201	-0.718772949
C	-0.879861755	4.583500618	-0.082726649
C	-1.356219432	5.610853249	-0.914215884
H	-2.422011670	5.817471999	-0.922224017
C	-0.508172774	6.343000817	-1.740337812
H	-0.910155175	7.124178023	-2.378226668
C	0.854379805	6.054296253	-1.745927043
H	1.533978497	6.607657766	-2.387863276
C	1.353013414	5.060075974	-0.903545889
H	2.420062452	4.869856516	-0.895382713
C	0.511902729	4.329091912	-0.040764358
P	1.221764143	2.920493239	0.920834590
Rh	0.760411193	0.990034416	-0.652504752
C	0.357476609	-0.568087472	-1.915502535
C	0.960364789	-0.926061387	-3.074392967
H	-0.468992886	-1.216177463	-1.626357134
H	0.567929676	-1.834994589	-3.541439040
C	2.113343858	-0.408694975	-3.822406654
C	2.719981130	0.786904285	-3.950382550
H	2.563642675	-1.186943963	-4.439495377
H	3.579185126	0.798078076	-4.621276146
O	1.334984159	2.242969300	-2.538472787
C	2.457980975	2.173495595	-3.442521864
C	3.719102407	2.793097777	-2.823452480
H	2.178392849	2.771587591	-4.325780501
O	2.913170832	0.459673594	-0.528808971
C	3.464877844	-0.649487650	-0.497207566
O	2.840933478	-1.781058841	-0.739162755
C	4.923988192	-0.809529301	-0.178491222
H	5.048596855	-1.549762172	0.617430377
H	5.354029943	0.146207656	0.117515302
H	5.444066669	-1.193928669	-1.061852733
H	3.568270683	3.857722219	-2.619254295
H	3.971740163	2.283813155	-1.890991320
H	4.564224563	2.710897873	-3.514188471
H	1.140888403	3.177816519	-2.368962295
H	1.939636485	-1.571976214	-1.095986165
H	0.418058029	0.089074250	0.532076177
C	2.955070821	3.413600541	1.339003246
C	3.382697367	4.745009270	1.478349983
H	2.715058242	5.567857245	1.247033715
C	4.672104472	5.034284716	1.925736981
H	4.985992969	6.069987214	2.020863678
C	5.548876252	4.003015470	2.263023284
H	6.550539546	4.231296876	2.615365131
C	5.125015002	2.678172444	2.159077714
H	5.792941206	1.869408155	2.442659682
C	3.840774793	2.385799898	1.699557129
H	3.519375060	1.353940837	1.629330435
C	0.499431512	2.973728910	2.617138766
C	0.495813768	4.161836156	3.366377896
H	0.826964541	5.092605542	2.915482712
C	0.076240359	4.159313839	4.694136320
H	0.078278579	5.086493987	5.260451684
C	-0.335854274	2.968098490	5.299058581
H	-0.655230057	2.966255092	6.337022185
C	-0.329117629	1.783006431	4.564477251
H	-0.644348682	0.852541949	5.028132892
C	0.086709183	1.784764610	3.230331639
H	0.093406785	0.857479922	2.664814799
C	-2.517323532	-0.150136475	-0.550789761
C	-2.177925907	-1.090762571	0.437301510
H	-1.308871628	-0.925353566	1.066595139
C	-2.943951040	-2.241098034	0.617518410
H	-2.667852339	-2.954136818	1.388986028
C	-4.057043677	-2.478274975	-0.193773733
H	-4.651233581	-3.376742868	-0.056850993
C	-4.396095466	-1.555488737	-1.182633300
H	-5.256529511	-1.731740334	-1.821530042
C	-3.635339434	-0.397199043	-1.360797441
H	-3.920285286	0.310613497	-2.131192953
C	-2.148403356	2.159745617	-2.285911840
C	-3.264444003	3.014882440	-2.285511677
H	-3.749976578	3.276841117	-1.351802795
C	-3.764535304	3.528300703	-3.482439898
H	-4.628791242	4.186223997	-3.463287348
C	-3.161240939	3.196571052	-4.697152811
H	-3.550447569	3.598394761	-5.628109637
C	-2.058801420	2.340985279	-4.706736267
H	-1.587973545	2.069286043	-5.647351436
C	-1.553083142	1.823852308	-3.512793155
H	-0.700055488	1.158461948	-3.534182160

==========

9 - Same as structure **12**, without acetic acid

==========

Rh	0.394191989	-0.146600475	-0.216205931
P	-0.720556633	-0.776186919	1.690065799
C	-1.894471574	0.560754557	2.200493727
C	-1.514950978	1.389641373	3.271626276
H	-0.599169138	1.182279123	3.812520529
C	-2.300716267	2.466022663	3.678779275

H	-1.978094277	3.081671448	4.513169734
C	-3.496957588	2.734251349	3.019864742
H	-4.123427635	3.566867575	3.325222164
C	-3.891117846	1.916707720	1.963130910
H	-4.823247778	2.122139463	1.446013121
C	-3.112273868	0.833231019	1.521907132
C	-3.189601137	-0.099013859	-0.890167909
C	-3.712354686	0.006872815	0.421369903
C	-4.940917433	-0.609385932	0.707080943
H	-5.352379137	-0.509778180	1.707414747
C	-5.634940210	-1.342505714	-0.252224580
H	-6.580529764	-1.811714147	0.003079452
C	-5.108507557	-1.462018454	-1.534716305
H	-5.637579388	-2.024068012	-2.298646610
C	-3.901133456	-0.837845558	-1.847268056
H	-3.521324556	-0.913147684	-2.859356816
P	-1.627221274	0.788610254	-1.337350175
C	1.970759122	0.933979972	-1.838401445
C	2.265605080	-0.396031781	-1.965704135
C	2.862628621	-1.214069094	-0.883088680
C	2.100684986	-1.207848820	0.221520947
H	1.459063355	1.430254311	-2.660603954
H	1.991324400	-0.884516545	-2.902047750
H	3.759426864	-1.809518487	-1.056814343
H	2.319392657	-1.812453831	1.099682025
C	2.904850480	3.213305113	-1.259373774
C	2.525010607	1.829552364	-0.748760239
H	3.689116675	3.134743679	-2.019474971
H	2.039763029	3.715578096	-1.703168441
H	3.289052681	3.838429947	-0.446427891
H	3.384707906	1.331166462	-0.290625570
O	1.476123054	1.936601512	0.267865191
H	1.868843619	2.212729650	1.107891082
H	-0.115825359	-1.467229115	-0.768164615
C	-2.143216783	2.550482826	-1.218853676
C	-1.263894227	3.506456042	-0.692327626
H	-0.288898586	3.198572043	-0.330776278
C	-1.647841483	4.847590337	-0.615993481
H	-0.961569507	5.581408296	-0.202723194
C	-2.908246813	5.244186633	-1.061456488
H	-3.205311687	6.287104192	-0.999442137
C	-3.791880340	4.295461014	-1.584136363
H	-4.775975724	4.598746439	-1.929813157
C	-3.414909500	2.956538350	-1.661014527
H	-4.111047635	2.226593482	-2.064192050
C	-1.430927480	0.492096973	-3.151810499
C	-1.596995082	1.511931116	-4.101860564
H	-1.879669944	2.510462166	-3.787355233
C	-1.408080374	1.253358396	-5.462796584
H	-1.541455722	2.056561155	-6.181628915
C	-1.058127439	-0.024327871	-5.898455205
H	-0.919055707	-0.223512231	-6.956667325
C	-0.889243459	-1.047125861	-4.961082242
H	-0.620618133	-2.047609568	-5.288075127
C	-1.063218620	-0.790377706	-3.601479262
H	-0.925263606	-1.596527767	-2.886501350
C	0.394605144	-1.004026453	3.144979346
C	1.533312381	-0.192479398	3.284310070
H	1.773244624	0.527909150	2.509858625
C	2.369078138	-0.316757352	4.393121909
H	3.244576002	0.319574042	4.483418285
C	2.087676411	-1.265668425	5.378394376
H	2.740849968	-1.369179550	6.239271990
C	0.968033800	-2.086238703	5.243741167
H	0.745306997	-2.832990675	5.999962133
C	0.125707848	-1.958976148	4.137730085
H	-0.736230837	-2.610554520	4.052226356
C	-1.662695420	-2.346174293	1.628195110
C	-2.787818929	-2.533143252	2.447906359
H	-3.159190611	-1.716321326	3.059360662
C	-3.438447409	-3.766126332	2.480077805
H	-4.311258729	-3.897114343	3.113199289
C	-2.971206015	-4.825713870	1.700834907
H	-3.480684643	-5.784567183	1.724936604
C	-1.847204304	-4.650744633	0.892163797
H	-1.475860214	-5.473250001	0.288069558
C	-1.194346153	-3.418898545	0.855373285
H	-0.315449583	-3.296721241	0.230344643

==========

9-TS - Reductive elimination transition state

==========

C	-0.176212268	0.215106483	0.145748651
H	-0.009589130	0.112070174	1.671901770
Rh	1.526932616	-0.041160859	1.378660044
P	1.278978154	-2.270920635	1.791937579
C	2.900244386	-3.075725129	2.153143618
C	3.525671904	-3.829083550	1.146877637
H	3.033762683	-3.964254894	0.190881861
C	4.764937686	-4.432485352	1.355070043
H	5.221729183	-5.013162311	0.559146428
C	5.399091584	-4.295844775	2.586103848
H	6.362578699	-4.763561503	2.766039109
C	4.786938491	-3.556384926	3.595581819
H	5.280421534	-3.447602430	4.556519399
C	3.546313618	-2.928262430	3.408302972
C	2.764729828	-0.819983640	4.676453872
C	2.976308599	-2.218107148	4.600867846
C	2.733058221	-2.999918433	5.741028050
H	2.907299307	-4.070306605	5.682510606
C	2.267574542	-2.440845134	6.929699273
H	2.083110222	-3.073829682	7.792442987
C	2.053095919	-1.067070898	6.998299994
H	1.700739585	-0.608711936	7.917798743
C	2.307064595	-0.268363149	5.882522864
H	2.158473587	0.802233574	5.962228345
P	3.112495337	0.259585180	3.212015014
C	2.225413109	2.082219118	0.166078755
C	0.908937082	2.263747753	0.467292419
C	-0.185839663	1.509798639	-0.210967364
H	2.968633597	2.607501112	0.763929789
H	0.654345145	2.942746742	1.281426139
H	-0.892551822	1.993053093	-0.885167239
H	-0.897322778	-0.520098275	-0.202256756
C	3.720878055	2.318253484	-1.835022975
C	2.734785030	1.415528103	-1.094239549
H	3.239132740	3.252656460	-2.139687800
H	4.579514526	2.559818731	-1.200645071
H	4.089336030	1.826284571	-2.742673247
H	1.880833894	1.180219481	-1.739802453
O	3.369438890	0.182994895	-0.688960831
H	3.756730522	-0.238431292	-1.469936648
C	2.828342134	1.979297087	3.828363078
C	3.877166673	2.879266343	4.070141242

H	4.906268277	2.570095703	3.923381522
C	3.609161329	4.179855650	4.506478041
H	4.434603564	4.862087475	4.688593911
C	2.295720360	4.600364374	4.713946487
H	2.092191679	5.609860513	5.058330868
C	1.242658513	3.712466652	4.476143593
H	0.215804975	4.028146604	4.638542470
C	1.505158463	2.417702221	4.028784268
H	0.679218367	1.736406836	3.842531271
C	4.944628551	0.135170928	3.047935877
C	5.541705099	0.199149437	1.780823176
H	4.920709425	0.277858795	0.894221278
C	6.932651751	0.148341612	1.655235426
H	7.384707378	0.196828851	0.668388872
C	7.740483976	0.030045132	2.786130755
H	8.821085919	-0.010891797	2.684866933
C	7.151666708	-0.039643505	4.051767384
H	7.772922424	-0.133446576	4.938083172
C	5.764542927	0.010775020	4.183707414
H	5.319955427	-0.047146056	5.172592902
C	0.158765713	-2.815463744	3.133408152
C	-0.788917283	-1.945525055	3.686986699
H	-0.828113210	-0.911032769	3.361271202
C	-1.671389686	-2.396162017	4.669874677
H	-2.399008203	-1.710776407	5.094450078
C	-1.615161116	-3.718549882	5.108748933
H	-2.301792474	-4.067689827	5.874426118
C	-0.669686473	-4.592451271	4.566681159
H	-0.618226489	-5.621940993	4.909155837
C	0.215086528	-4.145287057	3.587723754
H	0.954481205	-4.829456568	3.180953845
C	0.645046625	-3.092782572	0.268133988
C	1.150455009	-2.678415505	-0.978119787
H	1.877505016	-1.872782253	-1.020517855
C	0.716233735	-3.284925331	-2.155913055
H	1.120758735	-2.959742134	-3.110305682
C	-0.241958393	-4.301047554	-2.112200624
H	-0.583706007	-4.769510809	-3.030194600
C	-0.762611235	-4.703617172	-0.882781957
H	-1.514980402	-5.485609100	-0.838744242
C	-0.324128539	-4.106543170	0.301433541
H	-0.745119253	-4.433702095	1.245089190

==========

10 - Product complex

==========

C	0.397406711	0.138132527	0.562860332
H	0.747591593	0.300962087	1.577795488
Rh	2.559164926	-0.082072707	-0.482687389
P	2.301691828	-2.355125384	-0.676626079
C	3.616143641	-3.272541068	-1.599319660
C	3.345863873	-3.805760628	-2.869977744
H	2.358643719	-3.693061282	-3.301800764
C	4.319260829	-4.497657327	-3.592489706
H	4.078883282	-4.899323180	-4.572201261
C	5.586010719	-4.676133851	-3.043361718
H	6.354469618	-5.215992040	-3.588355011
C	5.863476166	-4.160649885	-1.777979048
H	6.850218369	-4.299489311	-1.346547552
C	4.905707704	-3.448940539	-1.038896213
C	5.406632090	-1.648904293	0.753670638
C	5.312751441	-3.001143651	0.334534800
C	5.705304238	-4.009297743	1.228888923
H	5.633424975	-5.043320648	0.905227764
C	6.170726885	-3.718880980	2.510157464
H	6.460021476	-4.523911488	3.178779015
C	6.269725343	-2.390681803	2.913764384
H	6.645112075	-2.139276869	3.901445014
C	5.894490134	-1.370652329	2.039071445
H	6.000747329	-0.342459938	2.364145696
P	4.870570568	-0.264722689	-0.356750598
C	2.539040265	2.398752833	-1.305561836
C	1.730314701	2.012406524	-0.261962335
C	0.632111260	1.066425836	-0.428664356
H	3.447785877	2.949456865	-1.070612518
H	2.013841443	2.291297469	0.750519978
H	0.106102750	0.991422845	-1.374877894
H	-0.332164591	-0.651083548	0.417715495
C	1.613727250	3.834998869	-3.106028929
C	2.153946112	2.435988082	-2.762682220
H	0.708737651	4.064495545	-2.536181851
H	2.366709905	4.599938958	-2.893368197
H	1.359736419	3.887103473	-4.171699838
H	1.374829284	1.690976994	-2.975763375
O	3.328017686	2.143887083	-3.514952988
H	3.174981194	2.416626868	-4.429357282
C	5.486410167	1.276159325	0.452419979
C	4.831016896	1.746458369	1.606249865
H	3.999189239	1.181925417	2.020023887
C	5.245382721	2.921157645	2.232032153
H	4.737002111	3.264515170	3.128595148
C	6.310222595	3.656291718	1.704572840
H	6.630913909	4.574397199	2.187939243
C	6.957891234	3.206304367	0.555142862
H	7.783878768	3.774883091	0.137790674
C	6.553212462	2.023308651	-0.068734559
H	7.069919396	1.688900757	-0.961265918
C	5.920906706	-0.475187341	-1.843816558
C	5.397664355	-0.227029082	-3.118321836
H	4.370121382	0.101825111	-3.226796656
C	6.210006157	-0.367314726	-4.245862735
H	5.798408480	-0.174807808	-5.232585681
C	7.544014494	-0.748949037	-4.109533871
H	8.173024999	-0.856361251	-4.988692620
C	8.072390047	-0.994268415	-2.839242369
H	9.111834541	-1.289333963	-2.727595421
C	7.265890202	-0.862959216	-1.711258814
H	7.681314916	-1.067017030	-0.728771824
C	2.079316785	-3.338145738	0.858496293
C	1.940829580	-2.694779058	2.095710301
H	1.999858524	-1.612431514	2.141681856
C	1.756562982	-3.436664128	3.263815869
H	1.655181141	-2.925722617	4.217044320
C	1.710220553	-4.829540275	3.207411193
H	1.565790364	-5.407105462	4.115798161
C	1.858634341	-5.481310775	1.979961163
H	1.830781771	-6.566088570	1.932793063
C	2.048263866	-4.743098745	0.812354274
H	2.177608378	-5.260326118	-0.134306423
C	0.762198072	-2.595795040	-1.663772223
C	0.607815607	-1.837529341	-2.839993131
H	1.402194906	-1.164001459	-3.152845128
C	-0.549715653	-1.946576425	-3.609054936
H	-0.647593403	-1.365043448	-4.521566664

C	-1.582225347	-2.798572677	-3.206460641
H	-2.486930045	-2.879129510	-3.801459452
C	-1.444448996	-3.541833988	-2.034416018
H	-2.243549056	-4.202874995	-1.711669437
C	-0.280340100	-3.445324665	-1.266364042
H	-0.192650919	-4.031976648	-0.358346878

Table S3*. Optimized structures of the initial complex and oxidative addition transition state for Cycle B (see Figure 4 in the main text).*

==========

3A - Rh(I)BIPHEP - acetylene + aldehyde adduct

==========

Rh	0.263710337	-0.188925662	-0.185528660
P	-0.700315801	0.423198793	1.909550518
C	-2.135846792	1.579379179	1.826965228
C	-1.999634620	2.895563584	2.296991898
H	-1.073812320	3.207287759	2.764507930
C	-3.038896622	3.818644701	2.188476120
H	-2.903082140	4.828980804	2.562846788
C	-4.244044429	3.434060679	1.608943355
H	-5.063913959	4.140287525	1.516513231
C	-4.398417876	2.126947685	1.154682968
H	-5.340599853	1.820609020	0.711638654
C	-3.363805733	1.183259141	1.244414187
C	-3.135764722	-0.891310254	-0.299619678
C	-3.702211089	-0.211344971	0.808414674
C	-4.742441608	-0.831617968	1.518495591
H	-5.175598044	-0.302676629	2.362194736
C	-5.226798605	-2.091201636	1.173761191
H	-6.029470687	-2.541958142	1.749240671
C	-4.677432670	-2.751209458	0.079037505
H	-5.048126536	-3.726236173	-0.223075934
C	-3.648360515	-2.151832989	-0.646727046
H	-3.254436153	-2.675290747	-1.508858820
P	-1.738806972	-0.165725741	-1.282898809
C	1.379434221	0.490724953	-1.931230752
C	1.480283796	-0.747408125	-1.945897025
H	1.482446473	1.514586321	-2.234313255
H	1.735928590	-1.741141405	-2.254313326
C	4.353490493	-0.732562097	1.803427511
C	3.236407407	-0.208271770	0.965051030
H	4.675052444	0.053716977	2.498436831
H	4.047791687	-1.620731521	2.358250620
H	5.217434780	-0.958346622	1.165782983
H	3.446513856	0.677193610	0.340847503
O	2.119515261	-0.714650478	0.947291493
C	-1.612026600	-1.252526117	-2.772847958
C	-1.986536696	-0.832574942	-4.056494376
H	-2.390390915	0.161002341	-4.212997480
C	-1.836345700	-1.686464266	-5.153643235
H	-2.127402666	-1.341369913	-6.141492043
C	-1.317861737	-2.969022505	-4.986369912
H	-1.208310093	-3.630961925	-5.840119141
C	-0.937384183	-3.396822598	-3.710908878
H	-0.530948227	-4.394211340	-3.568612246
C	-1.073653422	-2.543919616	-2.617221440
H	-0.759067942	-2.882339149	-1.633021345
C	-2.413501532	1.428488020	-1.898730610
C	-1.626104024	2.586424349	-1.884768003
H	-0.627539008	2.543730488	-1.462912256
C	-2.126115289	3.791047285	-2.384596164
H	-1.505950848	4.682597241	-2.363014262
C	-3.418419380	3.850318787	-2.906236900
H	-3.807623584	4.786249377	-3.296084504
C	-4.213851035	2.701269760	-2.918906133
H	-5.222652463	2.741524631	-3.319607188
C	-3.719431177	1.499766786	-2.414165099
H	-4.350500303	0.615240616	-2.422153759
C	0.576252674	1.358784464	2.860361252
C	1.330022444	2.337182963	2.186494782
H	1.140806710	2.527603594	1.132618418
C	2.308225291	3.070283354	2.857919772
H	2.870755947	3.833284047	2.326834556
C	2.562368204	2.825240764	4.211224647
H	3.323834206	3.394578432	4.735935272
C	1.828824638	1.847440795	4.883462272
H	2.020356759	1.649540689	5.934206316
C	0.840850212	1.118130669	4.215406097
H	0.278727972	0.363827818	4.755814012
C	-1.214521664	-0.938812246	3.027136379
C	-0.651831295	-2.211074768	2.846332877
H	0.050748071	-2.379404155	2.034368311
C	-0.988782756	-3.258356522	3.705389663
H	-0.549606472	-4.240471980	3.555914812
C	-1.889907989	-3.045628570	4.750248327
H	-2.154149987	-3.861675370	5.416300465
C	-2.454406725	-1.780927234	4.935623435
H	-3.156875206	-1.611409198	5.746733775
C	-2.121002761	-0.731051176	4.079544163
H	-2.569681818	0.247425498	4.227239118

==========

3A-TS - Oxidative addition transition state (acetylene-aldehyde coupling)

==========

C	0.246582771	-1.003288289	0.486454381
C	0.202634741	0.541740763	1.816511885
Rh	2.296293593	0.084189502	0.303344112
P	3.230619882	-0.391267251	-1.722422413
C	4.401969676	0.948281388	-2.209013952
C	4.015626087	1.898052548	-3.167673393
H	3.042784668	1.823799800	-3.638808330
C	4.868351811	2.933560138	-3.548666335
H	4.541208746	3.651767348	-4.294443996
C	6.134101357	3.030776356	-2.978140289
H	6.810839554	3.829071147	-3.267088079
C	6.534261241	2.086109222	-2.034367346
H	7.524135193	2.155336106	-1.593660062
C	5.691286361	1.041233814	-1.624570643
C	5.810146296	-0.206025689	0.647767934
C	6.277883141	0.044766934	-0.667382230
C	7.428888146	-0.629838474	-1.102813390
H	7.791678684	-0.439282800	-2.108365238
C	8.101030348	-1.539516913	-0.288825275
H	8.985443019	-2.047393862	-0.661975966
C	7.634548037	-1.786095062	0.998989036
H	8.150063850	-2.486314832	1.649327492
C	6.499943594	-1.119746567	1.459693997
H	6.153817208	-1.306609674	2.469816941
P	4.313540007	0.622063077	1.321313879

C	1.312027895	-1.677364039	0.202445960
H	-0.804377211	-1.149123450	0.266691612
H	1.607387452	-2.634610096	-0.201858969
C	-1.151752843	1.166241316	1.567042711
H	-1.312932448	1.920991168	2.346119288
H	-1.182485143	1.670636624	0.597939569
H	-1.959075584	0.431692077	1.630317740
H	0.230012530	-0.221451817	2.606886644
O	1.247721709	1.303400922	1.710217610
C	4.186086302	0.106568017	3.079411565
C	4.757544079	0.873676238	4.106322275
H	5.277748950	1.797152488	3.875306695
C	4.655285547	0.456313312	5.434481076
H	5.099850301	1.059997812	6.220194073
C	3.984102386	-0.724945134	5.753624230
H	3.905313015	-1.044722955	6.788315930
C	3.408483951	-1.490802151	4.737047272
H	2.879479082	-2.408269027	4.978349951
C	3.503610524	-1.076568638	3.408934839
H	3.039698583	-1.669319858	2.625461156
C	4.711817603	2.409502917	1.353065568
C	6.044144198	2.848531977	1.429858498
H	6.858122663	2.129993297	1.437032572
C	6.328962740	4.211907002	1.497662820
H	7.361457356	4.543526418	1.559811110
C	5.291333711	5.145948236	1.483214149
H	5.515842651	6.207550998	1.532031677
C	3.966212152	4.714142384	1.408776099
H	3.156987847	5.438477669	1.401996452
C	3.670758104	3.352194040	1.345424598
H	2.637495388	3.022932697	1.308807371
C	1.834785943	-0.339872118	-2.921123799
C	0.916758271	0.722777517	-2.819121462
H	1.072028427	1.506439251	-2.081979001
C	-0.196352112	0.779608660	-3.654603010
H	-0.890680067	1.610731819	-3.571783279
C	-0.420892059	-0.233381816	-4.590527749
H	-1.292301707	-0.193411575	-5.237408045
C	0.473828714	-1.297747204	-4.687102203
H	0.300788671	-2.091423516	-5.407926515
C	1.597105989	-1.354483060	-3.858726644
H	2.276713883	-2.194394419	-3.945294694
C	4.142101168	-1.945684347	-2.066201114
C	4.233547856	-2.970430281	-1.114937734
H	3.803407601	-2.833078108	-0.128631477
C	4.910013472	-4.154946761	-1.414200240
H	4.974858715	-4.939810526	-0.666346055
C	5.505290747	-4.327254203	-2.663962538
H	6.027603144	-5.250307664	-2.897041217
C	5.436506960	-3.302426889	-3.611826848
H	5.907584870	-3.424768616	-4.582816344
C	4.765151853	-2.117181927	-3.315810045
H	4.727427495	-1.324850164	-4.058242296

Table S4. *Vibrational frequencies of all structures in Table S2.*

==========

3 - Rh(I)BIPHEP bis-acetylene complex

==========

17.17 30.39 36.92 39.80 42.30 45.82
48.15 56.21 58.36 60.00 66.05 73.44
74.27 79.60 86.17 89.33 101.20 105.78
116.34 118.18 131.41 148.22 149.90 165.91
173.52 192.24 204.38 209.61 218.26 224.00
231.75 236.87 238.67 245.68 252.05 258.19
259.74 263.98 265.21 295.43 334.30 357.82
367.01 410.55 411.38 416.41 417.45 424.95
438.20 438.81 449.87 459.00 465.84 503.38
505.46 511.69 520.84 528.79 541.49 561.47
573.55 604.66 617.15 628.35 629.63 630.50
630.97 632.59 655.49 671.43 677.80 692.75
700.59 705.96 707.36 708.90 711.80 712.85
714.75 716.35 717.40 731.25 743.76 745.41
758.81 764.37 765.81 765.96 766.60 771.85
778.34 779.87 791.32 866.80 868.17 871.21
871.89 899.61 905.68 944.35 945.92 947.54
949.28 975.57 978.29 984.76 986.61 989.53
989.78 1008.12 1009.72 1010.78 1012.00 1012.03
1013.10 1015.75 1016.10 1016.87 1017.17 1017.37
1049.07 1050.00 1050.82 1050.87 1058.75 1061.43
1094.92 1104.48 1104.95 1109.10 1110.25 1111.54
1112.34 1113.34 1114.74 1118.66 1149.36 1163.11
1192.24 1192.45 1193.09 1193.66 1200.52 1202.66
1211.77 1212.24 1218.87 1219.72 1273.29 1293.74
1300.52 1323.34 1324.57 1325.80 1328.19 1330.15
1332.66 1358.54 1359.51 1363.36 1363.50 1466.86
1470.36 1473.98 1474.22 1477.59 1477.74 1503.35
1519.09 1522.97 1523.08 1525.38 1525.43 1612.65
1619.71 1625.51 1625.77 1627.35 1627.69 1636.70
1640.52 1641.55 1641.74 1642.30 1642.53 1941.48
1966.38 3172.83 3173.59 3184.84 3186.78 3188.64
3190.59 3190.99 3192.24 3192.85 3193.91 3197.77
3199.59 3199.74 3200.33 3200.61 3201.72 3203.91
3205.51 3212.37 3213.63 3213.81 3214.47 3214.57
3215.34 3224.04 3224.50 3237.31 3238.16 3388.33
3399.49 3472.76 3488.05

==========

3-TS - Oxidative addition TS

==========

-360.69 22.80 28.12 37.01 40.52 48.41
49.99 53.43 60.71 60.87 64.02 70.31
78.36 81.18 87.65 92.64 93.87 107.72
113.69 142.71 148.65 152.43 158.95 178.76
196.68 211.40 220.05 220.24 221.10 235.39
236.38 240.84 243.53 259.80 260.95 269.32
322.03 331.31 343.69 359.11 372.96 409.11
409.77 416.52 416.83 433.50 439.84 441.55
458.22 460.46 465.09 503.10 508.28 508.88
509.95 524.64 530.12 533.37 547.97 559.14
574.06 628.67 629.40 630.44 630.99 631.69
675.59 679.73 679.95 695.50 703.00 707.63
709.72 710.59 711.99 712.30 716.33 717.36
730.25 735.86 745.60 759.96 767.10 767.32
768.21 768.50 778.99 780.99 792.72 838.90
851.61 868.52 869.22 873.52 875.22 900.66
907.63 945.95 948.77 949.82 954.60 955.34
975.98 979.03 989.42 990.22 992.39 992.85
994.72 1009.81 1010.65 1011.56 1012.33 1012.63
1013.37 1017.44 1017.59 1018.02 1018.82 1019.02
1050.59 1050.83 1051.93 1052.06 1060.39 1063.18
1092.67 1107.02 1108.36 1111.60 1111.94 1113.51

1113.70 1114.35 1114.81 1117.49 1150.43 1163.65
1193.46 1194.51 1195.10 1195.32 1201.00 1201.86
1214.74 1215.07 1219.80 1220.35 1275.95 1295.64
1301.40 1325.00 1326.23 1328.36 1329.62 1331.54
1333.42 1361.46 1362.86 1365.12 1365.45 1468.71
1472.68 1475.10 1475.74 1478.64 1479.27 1502.68
1518.90 1523.69 1524.20 1525.02 1525.05 1612.83
1620.29 1626.20 1627.37 1628.21 1629.25 1638.22
1640.77 1641.56 1643.05 1643.43 1643.80 1686.87
1790.03 3182.48 3182.72 3186.55 3186.73 3191.64
3192.42 3192.60 3192.74 3193.21 3193.51 3200.31
3200.74 3200.93 3201.35 3201.66 3201.79 3207.73
3207.79 3212.38 3212.66 3212.83 3213.81 3214.52
3215.02 3222.85 3223.43 3226.44 3227.04 3297.41
3300.41 3343.79 3347.15

==========

4 - Rh-(III)-BIPHEP Rhodacyclopentadiene

==========

18.90 28.41 33.24 36.68 41.77 43.96
50.11 51.69 56.55 59.53 63.25 64.57
75.88 80.42 84.31 93.66 107.41 115.24
132.98 144.22 152.97 159.16 197.22 200.22
210.82 215.51 223.89 229.20 239.45 244.17
256.98 261.03 263.44 292.60 339.23 355.28
363.74 388.77 407.42 410.50 412.58 415.04
423.21 435.96 442.75 451.80 456.57 460.04
462.88 498.76 504.49 509.58 513.98 521.76
533.01 545.50 564.52 573.07 609.72 627.56
628.79 629.58 630.01 630.90 656.49 673.63
692.77 703.02 705.60 709.25 710.56 711.33
713.55 716.33 721.71 750.09 753.25 762.35
765.07 766.59 769.14 770.56 779.76 782.44
791.64 792.49 867.96 868.87 871.77 872.50
890.93 902.00 906.69 933.15 944.01 946.51
952.82 959.69 976.29 976.72 981.69 988.48
989.73 992.58 996.72 1008.88 1011.34 1011.68
1012.14 1012.18 1014.46 1015.16 1017.56 1019.78
1021.25 1021.67 1047.74 1050.52 1050.78 1051.98
1059.63 1063.40 1078.20 1091.87 1093.41 1107.96
1108.72 1110.12 1111.43 1113.68 1114.87 1116.42
1117.79 1119.71 1149.75 1161.72 1194.62 1195.05
1196.19 1196.40 1201.06 1203.91 1212.75 1217.32
1220.36 1222.96 1242.38 1266.32 1292.54 1298.73
1321.49 1326.24 1328.22 1329.71 1330.15 1332.26
1333.53 1361.37 1365.31 1366.15 1368.53 1464.34
1469.63 1476.73 1476.85 1478.19 1478.35 1500.54
1516.32 1523.97 1524.23 1525.30 1525.35 1564.39
1610.92 1617.07 1618.23 1625.18 1626.11 1626.92
1629.26 1635.96 1637.96 1640.38 1640.99 1641.03
1643.25 3140.70 3152.49 3165.98 3167.75 3168.90
3171.48 3186.80 3189.84 3191.34 3191.39 3193.41
3194.40 3195.32 3198.23 3199.26 3199.38 3201.58
3202.40 3203.85 3208.16 3209.36 3209.56 3211.17
3211.60 3212.54 3215.52 3215.79 3216.78 3218.11
3218.35 3225.45 3234.32

==========

5 - Rhodacyclopentadiene, aldehyde adduct

==========

17.74 25.90 28.34 33.23 41.09 44.94
48.22 53.89 58.42 61.23 65.31 68.52
73.93 76.04 77.51 84.28 85.49 97.60
102.15 112.71 126.96 134.43 142.25 148.46
153.80 163.58 178.88 191.72 203.05 213.95
217.58 219.12 226.67 229.01 239.03 243.16
254.14 257.62 260.43 265.83 330.24 338.26
353.89 363.75 389.82 407.85 412.33 414.39
416.47 422.84 438.19 442.55 458.34 459.24
462.93 475.71 503.49 510.41 512.97 513.65
520.29 525.83 533.08 542.50 564.38 573.94
604.27 626.81 629.24 629.91 630.23 631.58
668.79 673.13 689.87 700.72 706.64 709.08
709.33 710.41 711.47 714.99 718.44 749.79
761.59 764.98 765.81 766.80 769.39 771.10
776.43 779.64 790.77 793.10 794.40 863.41
868.00 871.46 876.85 897.57 900.09 904.87
911.01 940.39 943.70 949.37 955.57 956.90
975.50 978.42 985.47 987.54 987.58 994.19
997.74 1005.13 1008.97 1010.58 1011.68 1012.57
1012.94 1013.70 1015.72 1016.51 1018.27 1018.67
1043.76 1050.24 1051.79 1053.20 1056.48 1058.17
1085.66 1092.02 1103.88 1106.26 1108.40 1110.96
1111.76 1112.93 1113.41 1114.70 1115.61 1117.78
1134.69 1148.27 1156.11 1160.50 1192.86 1193.60
1194.15 1195.69 1199.65 1201.77 1213.04 1217.27
1222.52 1224.12 1248.90 1267.42 1292.89 1298.59
1320.28 1324.98 1325.84 1327.88 1328.53 1333.60
1344.29 1360.47 1362.29 1368.14 1369.48 1393.89
1438.58 1464.91 1465.97 1468.69 1473.28 1475.23
1475.88 1476.89 1478.91 1499.29 1514.87 1523.41
1524.43 1527.27 1528.11 1566.07 1610.75 1616.62
1621.72 1625.38 1626.25 1627.10 1629.18 1635.64
1637.54 1641.32 1641.66 1642.34 1644.67 1765.02
3007.41 3041.37 3095.74 3134.13 3146.71 3158.19
3164.15 3172.99 3183.02 3186.03 3187.99 3188.88
3190.15 3191.27 3192.40 3194.01 3194.31 3195.23
3198.02 3199.11 3199.97 3201.62 3203.26 3204.59
3209.64 3210.49 3212.25 3212.61 3213.43 3215.45
3220.27 3220.55 3220.84 3222.90 3237.34 3243.71

==========

5-TS - Aldehyde insertion TS

==========

-316.49 18.08 24.56 29.04 31.30 38.86
47.93 50.32 53.38 59.55 61.04 65.83
66.22 75.88 76.55 83.12 89.12 95.90
105.23 113.47 130.60 144.56 151.58 160.85
162.70 191.62 201.35 211.77 215.05 222.50
224.74 229.74 231.99 232.46 239.94 246.54
253.66 263.35 265.66 338.11 352.21 362.09
366.96 382.43 408.27 411.70 416.87 417.36
425.41 436.45 439.67 447.26 456.11 459.51
468.04 483.29 501.88 509.21 513.47 516.75
523.74 531.83 542.02 550.15 563.79 572.80
611.90 625.89 627.12 629.09 630.07 630.61
674.23 691.51 698.82 707.22 708.61 709.65
711.13 714.16 715.43 716.60 728.18 749.22
762.31 765.22 765.96 766.36 768.16 779.86
783.34 792.85 809.94 863.94 866.36 866.77
870.66 871.70 900.08 901.99 907.44 930.70
944.56 946.43 947.83 949.59 952.24 975.97
981.89 986.69 988.40 988.80 991.50 992.57
1005.96 1009.06 1010.68 1011.13 1013.05 1014.18

1015.98 1016.45 1016.71 1017.42 1019.07 1029.43
1045.22 1046.78 1050.18 1051.96 1060.43 1065.10
1077.27 1095.17 1106.17 1107.62 1107.98 1109.22
1110.09 1112.16 1113.51 1114.42 1115.83 1120.95
1126.03 1137.64 1149.80 1162.11 1192.88 1194.18
1194.55 1194.89 1200.55 1203.79 1213.84 1218.06
1220.46 1221.53 1266.66 1267.48 1292.34 1299.17
1318.74 1323.29 1325.65 1327.07 1330.07 1331.02
1334.17 1362.03 1362.58 1364.78 1366.25 1367.57
1405.33 1449.21 1464.36 1468.94 1473.93 1475.85
1476.23 1478.56 1483.38 1489.55 1503.14 1519.22
1523.76 1524.63 1524.72 1525.71 1526.84 1563.71
1612.87 1619.09 1624.57 1626.46 1627.53 1627.86
1638.33 1639.52 1640.18 1641.58 1643.09 1643.58
3038.96 3073.54 3116.44 3135.07 3157.32 3162.95
3166.76 3170.37 3172.33 3183.94 3187.88 3188.80
3189.67 3191.81 3192.12 3193.38 3196.37 3197.50
3198.98 3199.18 3200.52 3202.28 3204.69 3207.63
3211.61 3212.94 3213.08 3213.18 3213.97 3216.40
3218.26 3219.29 3221.76 3224.91 3228.52 3232.06

==========

6 - Aldehyde insertion product - Rhodacycloheptadiene

==========

15.74 28.12 31.19 33.81 37.59 44.22
45.99 50.83 55.56 58.29 61.44 67.14
68.00 70.59 77.78 81.83 90.11 103.71
111.10 123.48 131.95 153.02 156.27 165.72
188.81 204.62 206.86 213.07 220.34 230.13
234.61 240.73 247.41 253.51 258.56 262.59
269.41 275.68 315.53 335.54 355.85 371.62
374.70 407.05 409.63 413.60 415.80 426.13
435.35 442.00 447.49 455.63 462.44 464.82
495.04 505.23 510.38 515.17 517.48 525.26
533.77 548.31 559.85 573.31 576.71 628.40
628.94 629.86 630.33 631.27 657.39 678.27
695.39 700.47 706.16 708.77 710.43 711.96
713.04 718.28 718.54 722.68 747.35 762.76
764.42 765.27 766.52 768.82 769.59 781.21
783.99 793.75 815.33 844.16 860.02 866.76
872.01 880.63 903.77 909.99 910.77 927.88
944.50 947.87 953.71 962.54 966.83 980.54
983.45 985.47 988.68 991.86 1004.30 1009.72
1010.59 1011.76 1012.30 1013.13 1014.30 1015.97
1016.94 1017.31 1019.56 1019.95 1029.19 1046.25
1050.48 1050.94 1052.66 1052.70 1063.74 1066.30
1089.82 1094.67 1106.37 1107.97 1110.47 1111.51
1113.52 1114.38 1117.39 1119.41 1121.00 1151.57
1164.64 1172.18 1188.58 1194.78 1195.83 1196.43
1196.79 1201.87 1204.78 1216.68 1220.08 1221.10
1224.46 1270.19 1291.06 1299.29 1300.96 1306.45
1324.60 1326.91 1327.81 1331.26 1331.98 1332.47
1335.01 1353.36 1363.60 1367.74 1369.05 1371.82
1408.30 1454.94 1466.21 1470.65 1474.68 1477.88
1478.40 1478.75 1499.27 1502.50 1505.18 1516.41
1522.40 1525.52 1525.97 1526.47 1611.60 1618.96
1621.52 1623.24 1626.37 1628.34 1628.68 1637.79
1638.08 1640.13 1641.39 1642.10 1643.35 1695.25
2941.89 3035.38 3088.45 3107.85 3123.81 3138.30
3159.93 3163.83 3173.10 3181.07 3188.97 3189.72
3190.88 3191.87 3194.65 3194.68 3197.84 3199.73
3200.07 3200.80 3202.70 3204.98 3207.26 3209.42
3210.61 3211.76 3213.56 3213.95 3214.79 3216.50
3216.87 3217.68 3220.02 3224.30 3227.42 3248.61

==========

7 - Rhodacycloheptadiene with acetate, protonated

==========

-9.49 11.53 24.67 31.03 35.15 39.42
42.24 50.65 53.93 57.68 59.36 64.46
67.74 72.91 76.97 80.91 84.76 89.06
95.35 103.72 105.62 114.56 123.32 126.87
136.40 154.90 165.78 171.62 181.61 186.07
203.21 211.42 221.08 224.13 233.12 236.37
245.58 246.35 251.84 256.51 258.86 264.24
268.29 273.93 279.12 297.57 325.34 332.48
341.97 354.54 378.57 410.40 411.34 417.29
418.53 424.74 435.14 439.47 440.03 446.31
451.82 467.91 469.41 479.28 505.53 508.76
514.77 520.85 523.46 529.26 544.55 556.88
564.46 575.03 618.85 626.58 628.61 630.60
630.69 632.13 633.81 680.09 680.79 693.15
698.36 701.07 702.88 708.71 710.25 714.32
714.59 716.63 720.41 745.75 759.76 761.65
765.77 767.89 769.87 770.90 779.40 782.13
793.22 830.90 842.38 863.05 863.61 872.82
876.16 897.19 904.49 909.85 946.47 946.89
954.38 955.61 959.04 976.04 980.99 984.17
987.55 988.89 990.11 996.18 1002.95 1007.20
1008.87 1011.27 1011.97 1012.64 1013.02 1013.70
1015.78 1016.81 1018.48 1019.30 1022.36 1025.12
1030.40 1050.01 1050.20 1051.67 1052.07 1062.17
1064.37 1069.34 1093.75 1102.70 1105.33 1108.07
1109.77 1110.68 1111.98 1113.65 1115.73 1117.61
1119.22 1144.38 1151.12 1164.59 1194.14 1194.63
1195.19 1195.99 1201.67 1203.25 1221.36 1222.64
1224.92 1225.83 1228.52 1267.10 1274.36 1293.40
1300.95 1319.41 1321.48 1323.98 1325.02 1329.10
1330.98 1333.31 1353.94 1355.44 1366.51 1369.23
1369.79 1370.27 1392.12 1400.80 1423.66 1460.84
1464.96 1466.44 1471.47 1474.43 1475.80 1476.95
1477.75 1479.83 1499.29 1503.69 1503.89 1516.30
1517.97 1525.36 1526.82 1527.90 1528.33 1575.91
1610.23 1618.34 1625.55 1625.71 1627.31 1627.81
1638.89 1640.57 1640.97 1641.26 1641.77 1642.17
1643.14 1722.35 3007.71 3045.75 3061.79 3081.16
3116.75 3131.98 3133.09 3146.45 3150.46 3163.60
3172.87 3185.49 3188.17 3188.83 3189.69 3190.27
3192.70 3193.50 3195.82 3196.85 3199.05 3200.03
3200.90 3202.78 3208.78 3209.50 3210.81 3210.82
3212.44 3214.41 3215.35 3216.83 3222.87 3226.56
3228.09 3233.41 3236.65 3246.45 3247.30 3807.28

==========

7A'-TS - H2 activation TS

==========

-1187.28 8.87 18.43 27.39 32.52 33.73
35.97 41.99 48.61 50.32 54.53 58.02
63.03 66.13 69.05 71.72 76.41 78.08
81.54 86.01 92.04 96.78 100.83 113.75
115.23 118.23 130.40 131.66 140.62 151.20
155.78 159.96 174.72 187.56 193.44 207.86
211.88 220.36 223.86 232.25 237.95 241.96
248.17 251.29 252.85 262.59 265.24 267.45

269.71 285.89 312.26 339.48 356.86 366.15
368.43 393.17 408.27 411.26 412.24 416.95
423.49 429.02 442.08 445.81 452.49 458.44
468.92 472.65 492.02 503.60 508.00 514.98
518.59 525.54 534.39 547.18 550.29 563.44
571.54 575.73 619.50 627.95 629.18 629.78
630.21 632.73 646.78 667.44 677.65 681.67
694.38 702.58 706.48 708.58 709.89 713.26
715.34 716.32 717.67 732.54 746.94 761.00
768.89 769.06 769.63 771.49 776.22 778.90
781.98 787.31 792.39 830.69 868.85 869.62
873.35 879.53 901.44 906.93 928.18 941.72
947.13 951.64 952.25 957.03 959.79 977.20
978.99 982.26 990.85 991.22 991.96 996.48
1003.05 1004.78 1010.83 1011.21 1011.84 1012.96
1013.14 1013.48 1016.99 1017.57 1018.00 1018.18
1024.16 1032.74 1041.33 1048.67 1051.20 1053.05
1053.37 1061.60 1064.52 1071.32 1096.97 1105.10
1106.12 1110.20 1111.52 1111.88 1113.62 1114.66
1116.51 1117.30 1121.73 1151.69 1164.98 1175.15
1193.50 1193.83 1195.10 1195.40 1202.17 1203.83
1210.99 1212.40 1215.79 1221.87 1223.66 1227.30
1236.95 1252.22 1268.77 1278.65 1293.11 1301.72
1304.55 1319.53 1323.89 1326.01 1328.14 1329.54
1331.27 1333.14 1334.00 1362.15 1362.95 1365.53
1372.05 1372.53 1374.43 1394.65 1425.63 1455.54
1465.23 1466.66 1469.31 1474.99 1475.67 1477.34
1478.75 1483.11 1487.92 1495.96 1496.62 1503.64
1504.53 1518.46 1523.75 1524.99 1529.12 1529.39
1613.38 1620.42 1621.57 1625.69 1627.54 1629.15
1629.31 1637.95 1641.12 1641.61 1642.49 1644.06
1644.77 1645.76 1697.07 1702.48 1798.41 3068.97
3074.78 3077.63 3079.73 3129.15 3138.64 3139.27
3164.39 3181.70 3187.39 3187.43 3187.61 3189.20
3191.47 3192.98 3193.87 3194.61 3197.03 3197.83
3197.99 3199.25 3202.12 3202.39 3203.93 3206.15
3209.33 3211.72 3211.82 3212.22 3214.79 3215.69
3218.85 3220.27 3220.69 3223.59 3227.72 3228.14
3242.20 3244.83 3616.38

==========

7A' - rohdacycloheptadiene with acetate and H2 coordinated

==========

12.17 21.02 26.32 29.74 32.49 42.56
43.74 47.48 53.11 57.49 61.57 62.11
65.87 69.96 73.68 75.96 80.59 90.76
96.61 97.92 103.92 108.56 111.45 119.94
123.86 128.85 133.52 139.00 149.86 157.70
162.28 172.38 196.01 203.49 209.27 213.42
222.65 228.22 230.12 236.51 239.81 244.52
251.70 257.78 264.30 267.57 269.13 280.62
304.00 337.42 340.10 357.11 364.05 393.47
405.31 412.90 416.80 417.16 420.82 426.74
428.24 437.76 447.22 456.16 458.66 466.77
470.81 498.45 509.00 513.53 517.16 521.69
525.37 530.85 543.28 547.29 564.13 574.39
577.47 599.62 617.23 628.97 630.02 631.01
631.54 631.77 633.58 647.33 675.08 675.96
693.50 702.03 706.36 708.79 710.53 713.18
713.91 716.37 718.29 722.79 750.30 762.59
765.91 766.79 767.91 769.53 776.05 779.27
780.29 789.40 797.50 818.55 821.00 864.37
872.54 874.34 879.77 897.79 903.67 934.62
935.60 943.78 947.84 952.25 956.81 958.83
972.75 973.77 975.69 983.83 987.89 993.65
994.25 996.92 1002.38 1002.68 1005.68 1010.59
1010.85 1011.15 1014.22 1015.19 1018.03 1020.96
1028.57 1031.09 1040.77 1051.06 1052.58 1052.93
1053.34 1053.40 1060.57 1063.65 1064.67 1097.72
1107.69 1108.21 1110.41 1110.98 1115.88 1117.03
1117.49 1118.63 1121.47 1130.73 1139.96 1149.46
1162.09 1178.80 1191.02 1191.30 1191.61 1191.91
1199.22 1201.64 1205.54 1207.27 1219.41 1221.15
1223.01 1226.87 1227.02 1241.32 1267.27 1292.65
1300.25 1308.29 1319.84 1325.94 1327.49 1329.24
1330.38 1331.10 1335.01 1349.39 1359.83 1367.12
1370.17 1371.18 1372.75 1405.44 1437.57 1465.73
1467.65 1475.02 1475.71 1476.96 1477.41 1478.30
1481.12 1491.75 1494.29 1505.02 1511.22 1517.88
1527.99 1528.52 1530.36 1530.73 1613.89 1620.28
1627.38 1628.76 1629.60 1630.62 1634.30 1640.88
1643.41 1644.77 1644.94 1645.76 1646.58 1675.60
1700.09 1824.97 2940.46 3056.17 3056.27 3062.63
3117.73 3126.25 3129.80 3129.92 3158.46 3160.87
3173.45 3177.67 3177.90 3178.44 3178.92 3180.40
3182.60 3184.43 3189.39 3190.60 3191.35 3191.82
3193.63 3194.89 3200.80 3202.91 3203.05 3203.48
3206.06 3207.24 3208.31 3211.15 3213.07 3225.02
3231.29 3235.12 3236.13 3237.25 3242.87 3680.14

==========

8 - Protonated Rhodacycloheptadienehydride, acetic acid adduct (H2 activation product)

==========

19.16 24.70 31.05 38.99 41.54 44.20
47.76 49.84 54.10 54.85 60.74 61.65
67.29 69.64 71.99 79.93 83.58 88.89
91.92 96.11 100.04 113.27 117.51 127.58
137.44 145.12 158.07 166.70 169.85 182.14
190.13 196.90 205.79 210.55 216.79 224.78
233.95 235.35 239.30 249.38 252.15 257.68
262.37 263.96 264.93 285.09 331.65 337.17
354.86 370.95 386.52 408.24 410.75 416.23
417.99 425.24 429.15 438.36 440.62 449.85
456.22 459.44 465.00 468.29 484.53 501.83
514.00 518.56 523.62 529.27 539.53 559.95
563.06 577.25 588.52 627.83 628.93 630.24
630.97 631.64 633.14 635.69 677.03 691.82
699.47 701.84 706.45 707.75 708.50 709.29
712.11 712.90 717.03 750.17 751.83 760.09
761.34 768.48 769.23 770.24 774.49 776.62
779.27 781.10 796.25 827.85 834.87 853.04
859.60 866.76 868.92 870.34 901.18 903.61
912.34 913.30 937.70 947.11 948.52 953.88
976.58 979.48 981.00 982.52 988.98 993.48
994.25 1009.05 1010.30 1010.54 1010.80 1012.28
1013.11 1014.37 1014.74 1017.30 1017.60 1017.79
1018.11 1019.38 1039.28 1039.85 1047.14 1049.97
1051.32 1052.91 1057.02 1065.02 1071.05 1093.38
1104.60 1105.51 1107.00 1107.71 1109.69 1111.88
1112.42 1113.65 1114.20 1118.44 1148.67 1161.36
1164.18 1191.90 1194.18 1194.46 1194.61 1200.19
1202.86 1213.70 1219.76 1220.68 1221.99 1261.69
1268.87 1271.38 1294.30 1298.40 1303.17 1322.20

1324.19 1325.94 1328.12 1329.26 1332.93 1334.83
1351.84 1359.43 1362.56 1366.49 1367.80 1380.48
1397.40 1418.77 1422.63 1466.21 1469.59 1470.02
1472.22 1476.03 1476.54 1477.23 1478.02 1480.69
1488.59 1502.78 1508.57 1517.38 1518.88 1523.93
1524.39 1525.67 1527.93 1611.22 1613.81 1617.83
1625.84 1626.27 1628.07 1629.33 1638.75 1639.33
1641.19 1642.00 1642.69 1644.72 1716.11 1721.17
2227.38 2982.22 3057.75 3069.00 3081.80 3123.17
3129.94 3134.58 3150.26 3153.50 3158.45 3183.17
3185.36 3187.37 3187.50 3187.99 3189.67 3190.21
3191.13 3192.83 3195.20 3195.22 3197.08 3200.04
3201.41 3202.14 3203.10 3206.75 3208.73 3211.99
3213.04 3213.27 3213.49 3214.38 3216.80 3221.82
3222.20 3233.80 3241.74 3249.43 3352.15 3749.47

==========

9 - Same as structure 12, without acetic acid

==========

15.82 28.75 33.47 36.55 39.95 49.44
50.80 53.65 59.11 63.68 65.90 70.21
72.16 75.77 84.47 89.87 96.00 101.65
107.24 132.09 142.18 147.50 154.00 158.21
189.35 197.39 205.34 210.83 216.85 221.84
227.04 234.50 238.67 242.60 246.33 258.29
262.54 264.26 265.41 325.85 334.25 356.78
367.32 373.25 378.74 408.66 410.34 414.57
415.36 415.93 429.15 437.38 445.32 452.65
457.44 461.94 477.23 506.11 509.38 514.68
521.99 528.55 544.20 552.97 560.85 574.21
582.94 629.65 630.28 631.34 631.88 632.49
677.54 692.33 694.18 701.12 706.21 709.18
710.81 710.93 713.51 715.82 716.28 748.05
752.12 761.24 765.41 766.80 768.66 769.74
770.28 779.05 780.26 791.84 818.39 836.36
859.39 865.09 869.18 871.33 879.23 900.26
906.40 915.55 944.43 946.08 951.71 960.10
962.99 974.92 977.57 986.18 988.01 991.04
999.44 1000.64 1008.79 1009.74 1011.90 1012.76
1013.16 1014.40 1015.36 1017.08 1017.46 1018.13
1020.45 1020.90 1039.88 1051.32 1051.96 1052.16
1052.23 1059.61 1064.20 1093.53 1104.98 1106.77
1108.97 1110.19 1110.36 1112.04 1113.02 1113.78
1115.68 1116.63 1118.52 1134.27 1150.10 1163.01
1192.92 1193.94 1194.14 1194.94 1200.76 1202.40
1207.45 1217.27 1218.97 1219.26 1220.53 1268.18
1271.27 1292.29 1298.48 1300.46 1322.25 1323.30
1328.07 1328.20 1329.82 1333.39 1346.24 1362.52
1363.43 1363.62 1369.40 1389.31 1427.98 1444.26
1466.74 1470.76 1473.82 1476.18 1478.09 1479.18
1501.97 1502.16 1507.40 1516.52 1524.40 1524.63
1524.87 1528.39 1589.87 1611.38 1619.55 1624.16
1624.37 1626.90 1628.56 1629.29 1638.05 1640.87
1641.05 1642.62 1643.56 1644.69 2272.49 3049.37
3082.58 3122.57 3133.44 3139.59 3146.49 3177.09
3180.42 3183.69 3185.14 3187.27 3188.16 3191.25
3191.36 3192.95 3193.37 3194.02 3197.28 3199.62
3200.28 3200.54 3201.62 3202.31 3207.35 3210.18
3210.59 3212.12 3212.82 3214.15 3214.82 3217.94
3220.65 3221.24 3225.13 3225.37 3225.50 3802.49

==========

9-TS - Reductive elimination transition state

==========

-837.47 18.08 32.33 34.74 38.80 39.76
47.13 49.08 52.26 57.17 63.28 64.57
68.53 72.45 75.53 79.69 83.33 86.08
90.92 101.58 113.43 124.92 141.95 148.85
152.58 166.48 186.49 201.89 208.51 217.40
220.90 227.00 234.91 239.32 240.38 251.09
257.15 260.06 261.08 265.87 301.24 333.33
339.80 357.19 368.66 374.32 403.21 409.63
411.57 416.12 416.19 429.67 438.07 441.62
454.25 455.78 465.24 473.54 504.57 509.12
513.91 520.94 528.06 530.66 546.49 560.70
574.73 587.89 627.97 630.24 630.36 631.22
631.85 679.16 693.95 695.43 700.72 706.77
709.82 710.30 712.11 712.80 716.51 718.65
747.82 760.75 765.94 767.88 769.59 770.35
772.47 778.56 780.44 791.76 812.92 843.34
866.07 869.32 871.08 875.34 879.90 899.79
905.72 933.59 946.07 947.20 958.34 960.70
972.14 973.91 976.71 985.67 989.17 997.98
1001.19 1002.49 1007.78 1008.94 1010.06 1011.70
1012.52 1012.89 1016.25 1016.72 1017.49 1019.22
1019.54 1023.54 1048.32 1050.83 1051.03 1051.81
1051.85 1061.92 1063.28 1092.50 1107.62 1108.77
1109.10 1110.36 1110.52 1113.18 1114.27 1116.66
1117.33 1118.02 1118.71 1124.50 1150.51 1162.77
1192.83 1193.42 1194.77 1195.07 1199.73 1201.97
1215.82 1217.66 1220.51 1222.91 1223.75 1273.68
1274.20 1292.61 1294.41 1300.45 1323.91 1324.28
1327.16 1328.67 1331.07 1331.95 1358.74 1361.95
1362.47 1368.84 1370.11 1386.07 1425.53 1442.41
1468.65 1471.55 1474.15 1475.03 1477.79 1478.67
1501.76 1503.67 1508.45 1517.03 1523.61 1524.44
1526.55 1528.96 1603.89 1612.60 1619.31 1624.21
1625.46 1625.90 1628.05 1629.36 1638.69 1640.50
1640.57 1641.94 1642.81 1643.91 2044.90 3044.73
3059.69 3115.82 3132.96 3151.85 3155.17 3175.12
3180.42 3184.42 3185.99 3186.10 3189.30 3191.06
3191.39 3191.56 3191.69 3195.45 3195.80 3197.42
3198.15 3199.33 3201.28 3201.55 3201.95 3206.20
3208.57 3211.41 3211.47 3212.08 3212.41 3213.23
3214.09 3219.62 3224.03 3225.01 3225.49 3788.52

==========

10 - Product complex

==========

16.23 19.07 31.18 35.92 40.37 42.51
42.74 49.23 53.59 57.43 61.83 64.86
70.06 71.54 74.83 78.87 85.06 85.90
98.55 104.33 122.24 132.22 147.73 150.45
171.46 182.22 200.77 209.71 210.95 219.98
222.61 234.03 236.35 239.28 244.98 257.98
258.65 261.27 265.92 294.78 306.36 333.43
357.11 369.66 376.35 401.58 409.90 410.68
414.87 415.29 422.97 431.39 439.68 440.61
456.19 459.25 460.92 466.86 505.99 508.09
512.99 522.95 528.88 538.63 547.46 560.97
574.59 629.82 630.03 630.79 631.32 632.37
660.06 679.40 694.89 701.90 707.30 709.24
710.12 712.09 713.17 717.21 718.20 736.43
746.22 760.02 766.72 767.30 768.11 768.60

777.46 779.61 791.30 833.75 860.50 867.52
868.41 871.86 872.33 898.90 905.43 920.74
944.09 947.96 949.47 950.33 956.90 964.32
972.87 976.02 976.28 986.12 987.52 990.40
990.95 1001.06 1006.70 1007.70 1011.58 1011.86
1012.18 1013.32 1016.19 1016.34 1017.19 1017.25
1017.50 1046.55 1050.75 1051.39 1051.52 1052.51
1060.83 1061.77 1084.22 1092.12 1105.52 1108.26
1109.74 1111.06 1111.67 1111.91 1114.56 1116.17
1117.50 1128.99 1149.00 1161.86 1183.64 1192.70
1193.32 1193.67 1193.98 1199.13 1200.35 1211.90
1216.90 1217.53 1219.29 1238.60 1273.38 1279.02
1293.32 1296.08 1300.42 1322.90 1324.93 1325.48
1326.60 1330.31 1334.57 1352.08 1359.47 1362.70
1363.07 1364.20 1368.00 1410.05 1419.42 1467.18
1470.22 1470.76 1474.23 1475.18 1477.90 1479.23
1501.38 1503.94 1508.87 1516.46 1523.00 1523.45
1523.98 1527.72 1569.40 1611.40 1614.63 1618.41
1624.79 1626.24 1628.00 1631.14 1636.62 1639.32
1641.22 1641.95 1642.47 1644.54 3020.56 3042.35
3115.64 3139.03 3167.15 3173.50 3174.63 3177.08
3184.67 3185.84 3190.19 3190.83 3191.23 3191.37
3191.52 3191.56 3191.99 3197.98 3198.97 3199.09
3200.46 3200.48 3201.28 3209.00 3209.84 3210.64
3211.43 3211.68 3212.82 3213.17 3214.56 3218.96
3222.70 3223.26 3225.67 3227.53 3265.25 3815.77

Table S5. *Vibrational frequencies of all structures in Table S3.*

==========

3A - Rh(I)BIPHEP - acetylene + aldehyde adduct

==========

18.81 29.47 30.75 33.61 39.05 42.18
45.29 45.69 55.32 56.03 61.56 65.67
67.85 70.89 75.44 80.65 85.92 91.04
96.11 100.86 129.02 141.90 145.38 151.67
156.39 168.50 174.74 183.49 205.85 209.73
215.73 217.68 223.68 232.72 237.52 239.56
248.93 257.95 260.35 265.05 304.96 334.37
354.25 362.15 366.46 409.64 411.34 413.56
417.40 429.05 438.29 441.45 453.92 458.26
466.83 505.49 509.09 512.72 522.40 529.27
545.51 546.68 562.38 574.19 628.86 629.73
630.65 631.00 632.57 652.14 676.88 693.89
700.50 702.41 706.98 708.06 709.40 711.70
711.94 714.57 715.60 718.13 746.23 759.57
764.52 766.47 767.13 769.84 773.03 777.94
780.90 790.92 796.67 867.14 868.58 872.09
873.34 898.52 905.33 916.88 944.26 946.65
948.10 950.00 973.78 977.72 986.18 986.41
990.35 990.60 1007.75 1009.39 1011.70 1012.14
1012.48 1013.11 1015.36 1015.61 1016.40 1016.87
1017.63 1049.82 1050.09 1050.60 1051.14 1060.07
1064.69 1095.05 1103.90 1107.61 1108.52 1109.42
1111.11 1111.52 1114.46 1115.93 1119.64 1131.40
1150.63 1150.66 1163.26 1192.10 1192.32 1193.26
1193.35 1200.90 1202.11 1211.78 1214.77 1217.14
1219.40 1273.87 1294.54 1301.15 1324.45 1325.72
1326.10 1328.64 1330.67 1333.23 1359.28 1361.00
1362.09 1363.48 1389.82 1423.38 1465.43 1467.99
1470.81 1473.87 1473.96 1474.90 1477.56 1477.80
1503.65 1519.52 1523.57 1523.72 1524.36 1525.15
1613.61 1620.55 1624.81 1626.10 1627.50 1628.55
1639.68 1640.93 1641.49 1641.75 1642.02 1642.90
1765.70 1877.87 3015.29 3042.81 3100.91 3171.25
3172.55 3175.38 3182.48 3185.18 3186.68 3190.10
3190.85 3191.19 3191.68 3191.93 3195.91 3196.89
3198.93 3199.41 3199.96 3202.50 3202.73 3208.27
3209.88 3212.46 3212.96 3213.15 3213.99 3214.48
3217.01 3224.60 3231.71 3233.05 3353.95 3428.37

==========

3A-TS - Oxidative addition transition state (acetylene-aldehyde coupling)

==========

-390.82 19.04 30.04 30.95 36.95 41.41
45.35 50.77 51.64 55.95 59.83 66.80
68.22 71.43 78.13 85.24 88.40 98.05
104.61 116.58 134.29 148.64 150.26 161.53
189.32 205.51 209.12 216.58 220.93 226.70
230.74 235.51 238.46 242.96 257.70 262.57
265.78 280.45 293.02 332.53 358.63 366.32
371.29 408.26 409.67 410.93 417.72 435.04
441.01 443.99 453.83 459.37 467.65 482.12
508.02 510.54 511.99 523.06 524.06 530.05
544.98 559.63 569.53 574.96 628.01 628.89
629.13 630.45 631.27 678.31 680.22 696.08
703.99 707.96 709.75 710.08 711.78 715.73
717.87 719.48 746.17 760.50 765.89 767.09
767.30 769.25 778.83 779.18 781.84 792.44
848.71 867.81 868.72 872.47 875.21 901.01
907.29 908.09 945.26 949.65 950.65 957.07
961.83 976.14 976.83 979.01 989.78 990.49
996.05 996.63 1011.35 1011.63 1011.86 1012.23
1012.37 1013.70 1017.02 1018.36 1019.21 1019.82
1021.52 1050.31 1051.03 1051.76 1052.82 1062.52
1065.17 1077.19 1093.08 1107.37 1109.62 1110.89
1112.42 1113.72 1114.65 1115.38 1116.54 1118.79
1140.94 1151.53 1164.04 1194.12 1194.43 1195.81
1196.40 1201.79 1202.44 1214.75 1217.13 1220.83
1222.75 1273.14 1293.65 1300.91 1324.45 1326.52
1327.58 1328.13 1329.10 1332.26 1332.97 1361.54
1362.19 1365.89 1371.06 1405.39 1447.35 1468.35
1472.02 1474.96 1476.70 1478.76 1478.88 1489.10
1497.64 1501.63 1516.96 1523.56 1524.36 1525.43
1527.92 1612.06 1619.21 1626.23 1626.52 1628.18
1628.43 1637.70 1640.01 1641.32 1641.94 1642.81
1643.03 1660.89 3028.96 3050.73 3122.65 3150.07
3178.46 3182.84 3187.28 3187.46 3191.73 3192.96
3193.43 3193.72 3194.00 3195.44 3200.81 3201.13
3201.52 3202.21 3202.44 3203.59 3211.50 3211.65
3211.84 3212.29 3212.76 3214.64 3217.68 3218.16
3219.01 3223.38 3224.64 3227.00 3227.83 3283.10

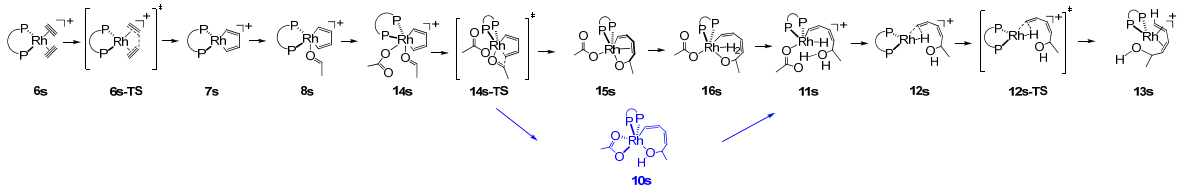
Table S6*. Computed energy components for the optimized structures of Cycles A and B (see Figure 2 in main text).*

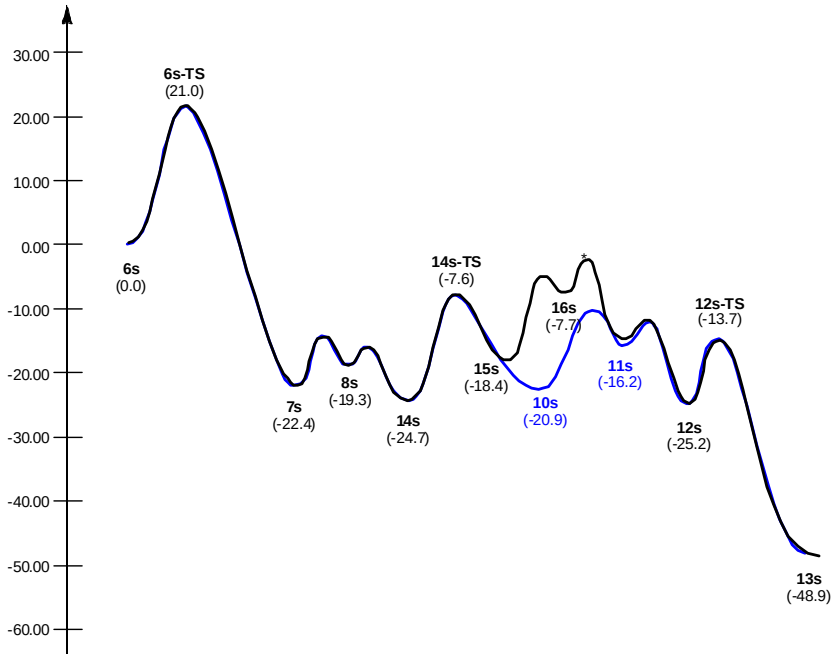
	E(SCF) (cc-pVTZ(-f)) (eV)	ZPE (eV)	-TS (298.15 K) (eV)	G gas (eV)	G(Solv) (eV)	ΔG(Sol) (eV)
Acetylene	-2105.089	0.729	-0.622	-2104.982	-0.162	-2105.144
Acetaldehyde	-4187.544	1.513	-0.811	-4186.842	-0.206	-4187.048
H_2	-32.109	0.277	-0.402	-32.234	0.000	-32.234
Acetic acid	-6236.155	1.685	-0.837	-6235.306	-0.339	-6235.645
Acetate	-6220.544	1.308	-0.892	-6220.128	-2.960	-6223.087
Methyl-2-oxoacetate	-9319.855	1.94	-1.03	-9318.948	-0.34	-9319.286
Cycle A:						
3	-63565.808	15.996	-3.154	-63552.966	-1.612	-63554.578
3-TS	-63565.388	16.061	-3.006	-63552.333	-1.555	-63553.888
4	-63567.076	16.201	-3.004	-63553.879	-1.636	-63555.515
5	-72887.780	18.238	-3.411	-72872.954	-1.639	-72874.5923
5-TS	-72887.509	18.212	-3.442	-72872.739	-1.623	-72874.362
6	-72888.804	18.331	-3.341	-72873.8145	-1.546	-72875.3609
7A	-79113.508	19.699	-3.664	-79097.4737	-0.841	-79098.3146
7A'	-79145.216	20.157	-3.704	-79128.7633	-0.954	-79129.7177
7A'-TS	-79157.258	20.461	-3.629	-79140.4269	-1.608	-79142.0344
8	-79157.805	20.618	-3.757	-79140.9448	-1.574	-74010.003
9	-72921.495	18.863	-3.436	-72906.0692	-1.560	-72907.6294
9-TS	-72920.925	18.782	-3.473	-72905.6168	-1.645	-72907.2616
10	-72922.405	18.91	-3.538	-72907.033	-1.653	-72908.6856
Cycle B:						
3A	-70780.925	17.215	-3.483	-70767.1933	-1.660	-70768.8528
3A-TS	-70780.165	17.264	-3.307	-70766.2084	-1.638	-70767.8463

Table S7*. Reaction energy profiles for other pathways considered.*

Note: In the following profiles, each structure label has the suffix "s" for small, to denote that these calculations were carried out using a small, truncated model of the BIPHEP ligand in which the four freely-rotatable phenyl groups were replaced by four protons to reduce the computational cost involved in this comprehensive exploration of all possible pathways.

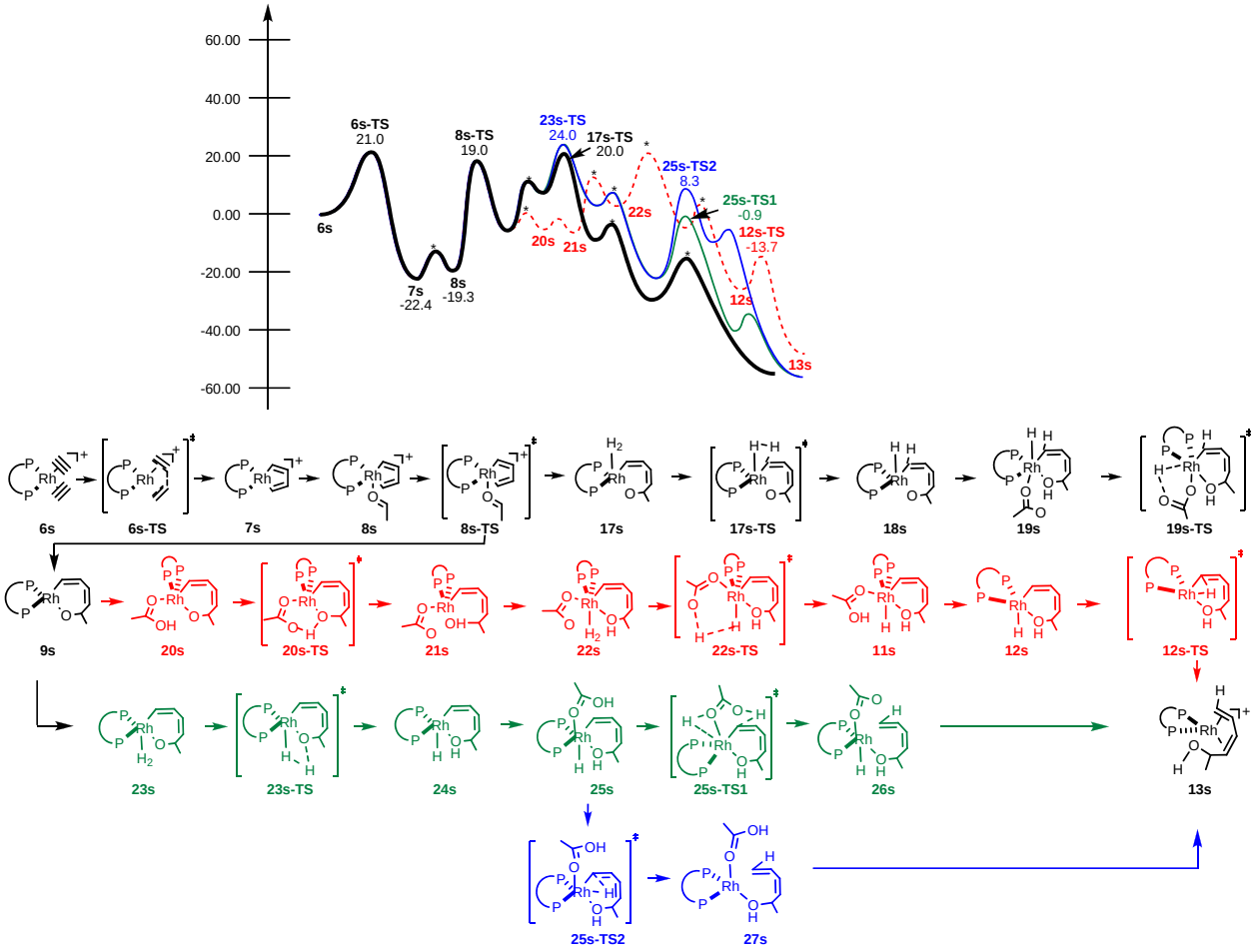
(I) Common pathway upto formation of Rhodacyclopentadiene – migratory insertion assisted by conjugate base of acid.





As a comparison with the full BIPHEP model discussed in the main text reveals, the qualitative mechanistic patterns are well reproduced with the small ligand model. However, significant quantitative differences exist. For example, the small phosphine model overestimates the oxidative addition barrier significantly, as **6s-TS** is computed to be 21 kcal mol^{-1}, which is much higher than the full model that gave 16 kcal mol^{-1}. Examining the transformation **6** → **7**, this disagreement becomes easy to understand: in **6s** the two acetylene moieties bound to Rh cause little to no steric tension, as the small phosphine ligands do not congest the ligand binding sites. However, in **6** the sterically demanding BIPHEP group causes significant sterically induced discomfort. In **6-TS**, on the other hand, the cyclization decreases the steric demand notably, as the two acetylene moieties have become a cyclobutadienyl fragment forming a metallacycle. Thus, the energetic penalty of having sterically demanding phosphine groups is less pronounced. As a result, the energy difference between **6** and **6-TS** compared to **6s** and **6s-TS** is significantly reduced.

(II) *Common pathway upto formation of Rhodacycloheptadiene – protonolysis vs. H2 activation.*



(III) Common pathway upto formation of Rhodacyclopentadiene - migratory insertion vs. H_2 activation.