Supporting Information

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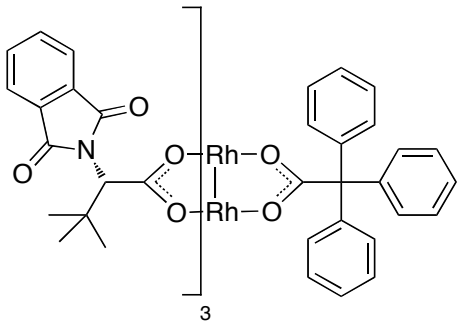
General Considerations

All non-aqueous reactions were carried out in glassware that was flame-dried under vacuum and cooled under nitrogen. CH_2Cl_2, toluene, diethyl ether, and hexanes were dried with columns packed with activated neutral alumina. THF was distilled from sodium/benzophenone. Chromatography was performed on silica gel (silicycle 40-63D, 60Å). For ^{13}C NMR, multiplicities were distinguished using an ATP pulse sequence: typical methylene and quaternary carbons appear 'up' (u); methine and methyl carbons appear 'down' (dn). NMR yields were determined by addition of 1 equivalent of mesitylene as an internal standard to the crude reaction mixture. GC yields were determined by addition of 1 equivalent of dodecane as an internal standard to the crude reaction mixture. Reagents were used directly as purchased from commercial sources without further purification. Ethyl 2-diazobutanoate, ethyl-2-diazopentanoate, ethyl-2-diazohexanoate were prepared from the corresponding commercially available corresponding β-ketoesters using a modification of a literature procedure.[1] Isobutyl-2-diazobutanoate and *tert*-butyl-2-diazo-3-phenylproprionate were prepared from the corresponding β-ketoesters using a modification of a literature procedure[7] (E)-1-phenylbutadiene was prepared according to a literature procedure.[2] Dirhodium tetrakis triphenylacetate,[3] dirhodium tetrakis N-phthaloyl (S)-tert-leucinate, dirhodium tetrakis N-2,3-naphthaloyl (S)-tert-leucinate, and dirhodium tetrakis N-1,8-naphthaloyl (S)-tert-leucinate were also prepared according to methods described in the literature[4]. X-ray quality crystals of Rh_2(*S*-PTTL)$_3$(TPA) were grown in ethanol. Enantiomeric excesses were measured on materials directly after chromatography (i.e. the reported ee's have not been enhanced through crystallization). The absolute configurations of cyclopropanes

reported in this paper are consistent with those reported in our previous work.[6] The absolute configurations of cyclopropenes reported in this paper are consistent with those reported in the literature.[7] The absolute configurations of functionalized indoles reported in this paper are consistent with those reported in our previous work.[8]

Experimental Procedures

One-Pot Preparation of Rh_2(*S*-PTTL)$_3$(TPA) (A)

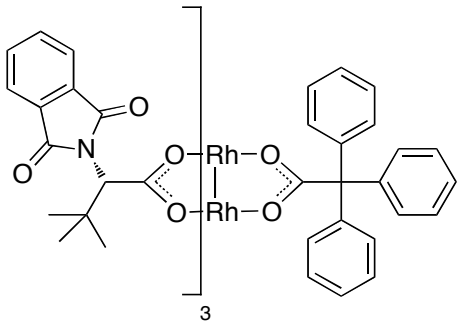


To a dry round-bottomed flask, fitted with an addition funnel containing sodium carbonate resting on glass wool and above it a reflux condenser, was added dirhodium tetraacetate (500 mg, 1.13 mmol), N-phthaloyl-(S)-tert-leucine (885 mg, 3.39 mmol), triphenylacetic acid (326mg, 1.13 mmol). The flask was evacuated and refilled with nitrogen three times, then chlorobenzene (12.6 mL) was charged via syringe through a septum. The reaction mixture was subsequently heated to reflux (165°C) in an oil bath under nitrogen atmosphere, and heating was continued for 20 hours, after which the chlorobenzene was removed by distillation at atmospheric pressure under nitrogen. The residue was dissolved in CH_2Cl_2 and washed twice with aqueous saturated sodium bicarbonate, dried over anhydrous $MgSO_4$, filtered, concentrated, and chromatographed on silica gel to give 576 mg (0.452 mmol, 40%) of the title compound as a green solid.

By-products were also isolated: Rh_2(*S*-PTTL)$_2$(TPA)$_2$ (0.226 mmol, 20%) and Rh_2(*S*-PTTL)$_4$ (0.452 mmol, 40%). Rh_2(*S*-PTTL)$_2$(TPA)$_2$ is a mixture of *cis*- and *trans*- isomers. Crystals of the *cis*-isomer were grown from CD_3CN and analyzed by x-ray diffraction.

Spectral properties of the chromatographed material: $[\alpha]^{20}_D$ = +802° (c. 0.28, CH_2Cl_2); ^{1}H-NMR (400 MHz, CD_3CN, δ): 7.89-7.74 (m, 12H), 7.34-7.20 (m, 9H), 7.02-6.97(m, 6H), 4.72 (s, 1H), 4.59 (s, 2H), 1.08 (s, 9H), 1.09 (s, 18H); ^{13}C-NMR (100 MHz, CD_3CN, δ): 193.8 (u), 188.6(u), 188.4(u), 172.0 (u – see unphased ^{13}C spectra), 145.6 (u), 135.6 (dn; 2 peaks), 133.1 (u), 132.9 (dn), 131.7 (dn), 128.6 (dn), 127.7 (dn), 124.5 (dn), 124.4 (dn), 70.2 (u), 62.1 (dn), 36.8 (u), 36.7 (u), 28.9 (dn), 28.7 (dn); IR (neat, cm^{-1}): 2961, 2928, 1774, 1735, 1686, 1654, 1603, 1385, 1265, 1108, 902, 788, 742, 671, 607; HRMS-ESI m/z: [M+Na], calc'd for $Rh_2C_{62}H_{57}N_3O_{14}Na$, 1296.1848 ; found 1296.1886.

Alternate Preparation of Rh_2(*S*-PTTL)$_3$(TPA) (A)



To a dry round-bottomed flask fitted with a reflux condenser was added dirhodium tetrakis triphenylacetate (100 mg, 0.0738 mmol) and N-phthaloyl-(S)-tert-leucine (67.4 mg, 0.258 mmol). The flask was evacuated and was refilled with nitrogen three times,

then chlorobenzene (14 mL) was charged via syringe through a septum. The reaction mixture was subsequently heated to reflux (165°C) in an oil bath under nitrogen atmosphere, and heating was continued for 20 hours, at which point the chlorobenzene was removed by distillation at atmospheric pressure under nitrogen. The residue was dissolved in CH_2Cl_2 and washed twice with aqueous saturated sodium bicarbonate, dried over anhydrous $MgSO_4$, filtered, concentrated, and chromatographed on silica gel to give 37 mg (0.029 mmol, 40%) of the title compound as a green solid. By-products were also isolated: Rh_2(*S*-PTTL)$_2$(TPA)$_2$ (0.014 mmol, 20%) and Rh_2(S-PTTL)$_4$ (0.029 mmol, 40%). Rh_2(*S*- PTTL)$_4$ was later combined with triphenylacetic acid in chlorobenzene and heated to reflux to give an additional 17% yield of Rh_2(*S*-PTTL)$_3$(TPA), for a combined yield of 57%, and Rh_2(*S*-PTTL)$_4$ as recovered starting material.

General procedure 1 for cyclopropanation to provide racemic products

In a dry round bottomed flask, Rh_2TPA_4 (2.8 mg, 0.0021 mmol)) and the appropriate alkene (0.409 mmol) were dissolved in anhydrous CH_2Cl_2 (3.00 mL) and cooled by a bath of dry ice/acetone (−78°C) under nitrogen atmosphere. The appropriate diazoester (1.23 mmol) was dissolved in anhydrous CH_2Cl_2 (1.50 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. Upon completion of addition, the mixture was allowed to warm to room temperature. The solvent was subsequently removed under reduced pressure, and the residue was chromatographed on silica gel. NOTE: Compounds 1, 2, 3, 4, 7, and 8 were prepared according to previously described protocols.[5]

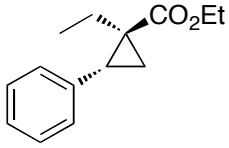
General procedure 2 for cyclopropanation to provide nearly racemic products

In a dry round bottomed flask, a 1:1 mixture of Rh_2(*S*-PTTL)$_4$ and Rh_2(*R*-PTTL)$_4$ (0.0021 mmol)) and the appropriate alkene (0.41 mmol) were dissolved in anhydrous CH_2Cl_2 (3.0 mL) and cooled by a bath of dry ice/acetone (−78°C) under nitrogen atmosphere. The appropriate diazoester (1.2 mmol) was dissolved in anhydrous CH_2Cl_2 (1.5 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. Upon completion of addition, the mixture was allowed to warm to room temperature. The solvent was subsequently removed under reduced pressure, and the residue was chromatographed on silica gel.

General procedure for enantioselective cyclopropanation using Rh_2(*S*-PTTL)$_3$(TPA)

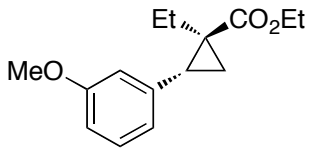
In a dry round bottomed flask, Rh_2(*S*-PTTL)$_3$(TPA) (1.0 mg, 0.0082 mmol) and the appropriate alkene (0.16 mmol) were dissolved in anhydrous hexanes (1.2 mL) and cooled by a bath of dry ice/acetone (−78 °C) under nitrogen atmosphere. The appropriate diazoester (0.82 mmol) was dissolved in anhydrous hexanes (0.6 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. After the addition was complete, the mixture was allowed to warm to room temperature. The solvent was subsequently removed under reduced pressure, and the residue was chromatographed on silica gel.

(1S,2R)-(+)-Ethyl 1-ethyl-2-phenylcyclopropane-1-carboxylate (1)



The general procedure for enantioselective cyclopropanation was followed with ethyl 2-diazobutanoate (82 mg 0.58 mmol) and styrene (20.0 mg, 0.19 mmol) to give 39 mg (0.18 mmol, 92%) of known compound **1** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. The diastereomer ratio was measured to be 96:4 by GC analysis. The enantiomeric excess of the major diastereomer was measured to be 88% ee by HPLC analysis (CHIRACEL OD column, 0.1% 2-propanol in hexanes, 1 mL/min, 220 nm). A repetition of that experiment gave **1** in 90% yield. $[\alpha]^{20}_{D}$ = +47° (c. 1.04 $CHCl_3$); The spectral properties were identical to those previously described in the literature for the racemic material.[5]

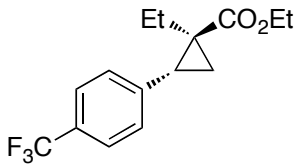
(1S,2R)-(+)-Ethyl 1-ethyl-2-(3-methoxyphenyl)cyclopropane-1-carboxylate (2)



The general procedure for enantioselective cyclopropanation was followed with ethyl 2-diazobutanoate (266 mg, 1.87 mmol) and 3-methoxystyrene (50.0 mg, 0.373 mmol) to give 78 mg (0.37 mmol, 85%) of the title compound as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. The diastereomer ratio was measured to be 99:1 by GC analysis. The enantiomeric excess was measured to be 90%ee by HPLC

analysis (CHIRACEL OJ-H column, 0.1% 2-propanol in hexanes, 1mL/min, 254 nm). A repetition of that experiment gave **2** in 83% yield. . Spectral properties of the chromatographed material: $[\alpha]^{20}_{D}$ = +85° (c. 0.077 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (app t, J = 7.9 Hz, 1H), 6.82 – 6.70 (m, 3H), 4.24 – 4.09 (m, 2H), 3.80 (s, 3H), 2.78 (dd, J = 8.8, 7.3 Hz, 1H), 1.70 – 1.57 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.13 (dd, J= 7.1, 4.7, 1H), 0.96-0.83 (m, 4H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0(u), 159.52(u), 138.9(u), 129.2(dn), 121.8(dn), 115.3(dn), 112.0(dn), 60.8(u), 55.3(dn), 32.5(dn), 31.5(u), 21.9(u), 18.1(u), 14.4(dn), 11.9(dn). IR (neat, cm^{-1}): 2975, 2937, 1716, 1602, 1583, 1491, 1456, 1379, 1313, 1242, 1155, 1044, 783, 716, 693; HRMS-EI (70-VSE) m/z: [M^+], calc'd for $C_{15}H_{20}O_3$, 248.14125, ; found 248.14150.

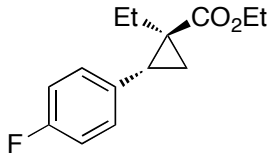
(1S,2R)-(+)-Ethyl 1-ethyl-2-(4-(trifluoromethyl)phenyl)cyclopropane-1-carboxylate (3)



General procedure for enantioselective cyclopropanation was followed with ethyl 2-diazobutanoate (74 mg, 0.52 mmol) and 4-(trifluoromethyl)styrene (30 mg, 0.17 mmol) to give 49 mg (0.17 mmol, 98%) of the title compounds as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. The diastereomer ratio was measured to be 97:3 by GC analysis. A repetition of that experiment gave **3** in 95% yield. The enantiomeric excess of the major diastereomer was measured to be 97%ee by HPLC analysis (CHIRACEL OF column, 0.1% 2-propanol in hexanes, 1mL/min, 220 nm). Spectral properties of the chromatographed material: $[\alpha]^{20}_{D}$ = +63.6° (c. 0.11 $CHCl_3$); ^{1}H

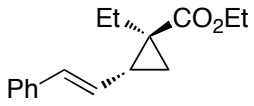
NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.26-4.13 (m, 2H), 2.84 (app t, J = 8.0 Hz, 1H), 1.69 (dd, J = 9.0, 4.8 Hz, 1H), 1.64 – 1.53 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.19 (dd, J = 7.1, 4.8 Hz, 1H), 0.96 – 0.79 (m, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6(u), 141.5(u), 129.7(dn), 129.0(u; q, J_{CF}=32.5Hz), 125.2(dn; q, J_{CF}=3.7Hz), 124.4 (u; q, J_{CF}=272Hz) 61.0(u), 31.9(dn), 22.0(u), 18.2(u), 17.5(u), 14.4(dn), 11.8(dn). IR (neat, cm^{-1}):2979, 2938, 2880, 1719, 1620, 1498, 1382, 1326, 1243, 1165, 1123, 1071, 1050, 1018, 846; HRMS-EI (70-VSE) m/z: [M^+], calc'd for $C_{15}H_{17}F_3O_2$, 286.11807, ; found 286.11893.

(1S,2R)-(+)-Ethyl 1-ethyl-2-(4-fluorophenyl)cyclopropane-1-carboxylate (4)



General procedure for enantioselective cyclopropanation was followed with ethyl 2-diazobutanoate (117 mg, 0.820 mmol) and 4-fluorostyrene (20 mg, 0.16 mmol) to give 37 mg (0.16 mmol, 96%) of known compound **4** as a colorless oil. The purity was measured to be ≥ 95% by ^1H NMR and GC. The diastereomer ratio was measured to be 97:3 by GC analysis. Enantiomeric excess was measured by reducing **4** to the corresponding alcohol **4a**. A repetition of that experiment gave **4** in 93% yield. $[\alpha]^{20}_D$ = +21° (c. 1.0 $CHCl_3$); The spectral properties were identical to those previously described in the literature for the racemic material.[5]

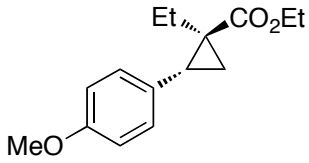
(1S,2R)-(+)-Ethyl 1-ethyl-2-(E)-(β)-styrylcyclopropane-1-carboxylate (5)



General procedure for enantioselective cyclopropanation was followed with ethyl 2-diazobutanoate (109 mg, 0.770 mmol) and (E)-1-phenylbutadiene (20 mg, 0.15 mmol) to give 31 mg (0.13 mmol, 82%) of the title compound as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and HPLC. The diastereomer ratio was measured to be 78:22 by HPLC analysis. The enantiomeric excess of the major diastereomer was measured to be 79% ee and the minor diastereomer 66% ee by HPLC analysis (CHIRACEL IA column, 0.1% isopropanol in hexanes, 1 mL/min, 220 nm). A repetition of that experiment gave **5** in 82% yield. Author's note: In the LC spectrum of the racemic material, there exists an inseparable impurity eluting at approximately 11 mins, just before the peak at 11.47 mins, with a UV spectrum which does not match the other peaks. This impurity is not observed in the enantioselective preparation of this compound. Spectral properties of the chromatographed material: $[\alpha]^{20}_{D}$ = +35° (c. 0.50 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ) of the major diastereomer: 7.34-7.27 (m, 4H), 7.23-7.16 (m, 1H), 6.59 (d, J = 15.9 Hz, 1H), 6.00 (dd, J = 15.7 Hz, 8.5 Hz, 1H), 4.24-4.10 (m, 2H), 2.40-2.20 (m, 1H), 1.68 (app q, J = 7.2 Hz, 2H), 1.30 (t, 3H), 1.05 (t, J=7.1 Hz, 3H), 0.88 (dd, J = 6.6 Hz, 4.4 Hz, 1H); Peaks at 6.14 ppm, 5.98 ppm, 2.16-2.07 ppm, 1.91-1.84 ppm, 1.68 ppm, 1.61-1.58 ppm, 1.28ppm, and 1.08 ppm were attributed to the minor diastereomer. ^{13}C NMR (100 MHz, $CDCl_3$, δ): 174.8(u); 172.8(dn); 137.6(u); 132.4(dn); 131.1(dn); 128.7(dn); 128.6(dn); 128.3(dn); 128.1(dn); 127.4(dn); 127.1(dn); 126.1 (dn); 126.6(dn); 60.8(u); 33.7(u); 32.2(dn); 31.9(u); 30.4(dn);28.7(u); 22.7(u); 21.9(u); 20.9(u); 14.5(dn); 14.4(dn); 12.4(dn); 11.9(dn); IR (neat, cm^{-1}): 2976, 2935,

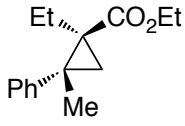
1716, 1450, 1309, 1239, 1154, 1039, 962, 752, 693; HRMS-ESI m/z: [M+H], calc'd for $C_{16}H_{20}O_2$, 245.1542, ; found 245.1536.

(1S,2R)-(+)-Ethyl 1-ethyl-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (6)



The general procedure for enantioselective cyclopropanation was followed with ethyl 2-diazobutanoate (266 mg, 1.87 mmol) and 4-methoxystyrene (50.0 mg, 0.373 mmol) to give 92 mg (0.37 mmol, 99%) of known compound **6** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. The diastereomer ratio was measured to be 92:8 by GC analysis. The enantiomeric excess of the major diastereomer was measured to be 81%ee by HPLC analysis (CHIRACEL OJ-H column, 0.1% 2-propanol in hexanes, 1mL/min, 230 nm), and this was confirmed by synthesizing (1R,2S)-**6** using Rh_2(*R*-PTTL)$_3$(TPA) as catalyst to show the opposite enantioselectivity. A repetition of that experiment gave **6** in 98% yield. $[\alpha]^{20}_D$ = +66° (c. 1.0 $CHCl_3$); The spectral properties were identical to those previously described in the literature for the racemic material.[5]

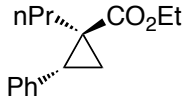
(1S,2R)-(+)-Ethyl 1-ethyl-2-methyl-2-phenylcyclopropane-1-carboxylate (7)



General procedure for enantioselective cyclopropanation was followed with ethyl 2-diazobutanoate (240 mg, 1.64 mmol) and 1-methylstyrene (20 mg, 0.17 mmol) to give 21 mg (0.090 mmol, 53%) of known compound **7** as a colorless oil. The purity was

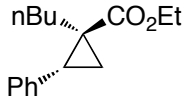
measured to be ≥ 95% by ^{1}H NMR and GC. The diastereomer ratio was measured to be (84:16) by GC analysis. The enantiomeric excess of the major diastereomer was measured to be 90% ee by HPLC analysis (CHIRACEL OF column, 0.1% isopropanol in hexanes, 1 mL/min, 220 nm). A repetition of that experiment gave **7** in 53% yield. $[\alpha]^{20}_D$ = +12° (c. 1.0 $CHCl_3$); The spectral properties were identical to those previously described in the literature for the racemic material.[5]

(1S,2R)-(+)-Ethyl 1-n-propyl-2-phenylcyclopropane-1-carboxylate (8)



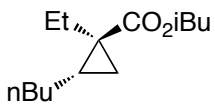
The general procedure for enantioselective cyclopropanation was followed with ethyl 2-diazobutanoate (90 mg 0.58 mmol) and styrene (20 mg, 0.19 mmol) to give 45 mg (0.18 mmol, 92%) of known compound **8** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. The diastereomer ratio was measured to be 99:1 by GC analysis. The enantiomeric excess was measured to be 95% ee by HPLC analysis (CHIRACEL OD column, 0.1% 2-propanol in hexanes, 1 mL/min, 220 nm). The racemate for this compound was reported in our previous work.[6] A repetition of that experiment gave **8** in 92% yield. $[\alpha]^{20}_D$ = +24° (c. 0.14 $CHCl_3$); The spectral properties were identical to those previously described in the literature for the racemic material.[5]

(1S,2R)-(+)-Ethyl 1-n-butyl-2-phenylcyclopropane-1-carboxylate (9)



The general procedure for enantioselective cyclopropanation was followed with ethyl 2-diazohexanoate (98 mg, 0.58 mmol) and styrene (20 mg, 0.19 mmol) to give 44 mg (0.18 mmol, 93%) of known compound **9** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. The diastereomer ratio was measured to be 99:1 by GC analysis. The enantiomeric excess was measured to be 96% ee by HPLC analysis (CHIRACEL OD column, 0.1% 2-propanol in hexanes, 1 mL/min, 220 nm). The racemate for this compound was reported in our previous work.[6] A repetition of that experiment gave **9** in 93% yield. $[\alpha]^{20}_{D}$ = +56° (c. 0.15 $CHCl_3$); The spectral properties were identical to those previously described in the literature for the racemic material.[5]

(1S,2R)-(+)-Isobutyl 1-ethyl-2-n-butylcyclopropane-1-carboxylate (10)



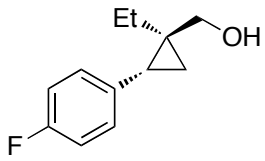
General procedure was followed with isobutyl 2-diazobutanoate (198 mg, 1.16 mmol) and 1-hexene (20 mg, 0.23 mmol) in hexanes (1.16 mL) to give 33 mg (0.15 mmol, 64%) of the title compound as a colorless oil after chromatography on silica gel deactivated with $EtSiCl_3$[10]. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. The diastereomer ratio was measured to be 72:28 by GC analysis. A repetition of that experiment gave **10** in 63% yield. Enantiomeric excess was measured by reducting **10** to alcohol **10a**. Spectral properties of the chromatographed material: $[\alpha]^{20}_{D}$ = +18° (c. 0.017 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$ δ): 3.86 (d, J = 6.6 Hz, 1H), 3.82 (d, J = 6.5 Hz, 2H), 1.92 (ddd, J = 19.8, 13.3, 6.7 Hz, 3H), 1.86 – 1.75 (m, 3H), 1.49 (dd, J = 12.8, 6.6 Hz, 2H), 1.45 – 1.19 (m, 13H), 1.02 (t, J = 7.3 Hz, 3H), 0.98 – 0.80 (m, 11H), 0.33 (dd, J = 6.5, 3.8 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$ δ) for the major diastereomer: 176.1(u),

70.7(u), 32.0(u), 29.2(u), 28.8(u), 28.3(u), 27.9(dn), 22.7(u), 21.8(u), 21.0(u), 19.3(dn), 14.2(dn), 12.6(dn). ^{13}C NMR (100 MHz, $CDCl_3$ δ) for the minor diastereomer: 70.8(u), 29.4(dn), 29.0(u), 27.7(dn), 22.6(u), 21.0(u), 19.5(dn), 19.4(dn),14.3(dn), 12.1(dn). IR (CH_2Cl_2, cm^{-1}): 3450, 2966, 1715, 1640, 1460, 1383, 1264, 1150, 1067 ; HRMS-EI (70 - VSE) m/z: [M^+], calc'd for $C_{14}H_{26}O_2$, 226.19328 ; found 226.19251.

General procedure for ester reduction

To a dry round bottomed flask was added 0.39 mL (0.39 mmol) of a 1.0 M solution of diisobutylaluminium hydride in THF. The mixture was cooled by a bath of dry ice/acetone (−78 °C), and 0.10 mmol of the cyclopropane carboxylic ester in 0.7 mL anhydrous THF was added dropwise. The reaction mixture was then warmed to room temperature and allowed to stir for 1 hour. The flask was then cooled by a bath of ice water (0 °C) and 161 mg (0.50 mmol) $Na_2SO_4 \cdot 10H_2O$ was added and the mixture was allowed to warm to room temperature and stir for 30 minutes. The mixture was then filtered, concentrated, and chromatographed on silica gel.

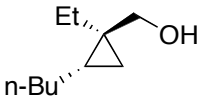
(1S,2R)-(+)-1-Ethyl-2-(4-fluorophenyl)cyclopropylmethanol (4a)



General procedure was followed starting with **4** (17 mg, 0.072 mmol) and a 1.0 M diisobutylaluminium hydride solution (0.18 mL, 0.18 mmol) to give 7.3 mg (0.038 mmol, 53%) of **4a** as a colorless oil. The purity was measured to be > 95% by ^{1}H NMR.

The enantiomeric excess of the major diastereomer was measured to be 95% ee by chiral GC analysis (G-TA column, 50-180°C, 2°C / min, flow rate 1 mL/min). A repetition of that experiment gave **4a** in 52% yield. Spectral properties of the chromatographed material: $[\alpha]^{20}_{D}$ = +0.4° (c. 0.50 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.15-7.11 (m, 2H), 6.98-6.93 (m, 2H), 3.68 (d, J = 11.2 Hz, 1H), 3.46 (d, J = 11.2 Hz, 1H), 2.05 (dd, J = 6.2, 8.6 Hz, 1H), 1.48-1.18 (m, 3H), 1.03-0.93 (m, 1H), 0.89-0.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 161.4 (u; d, J_{CF}=243 Hz), 134.5 (u; d, J_{CF}=3.2 Hz), 130.6 (dn; d, J_{CF}=7.9 Hz), 114.9 (dn; J_{CF}=21.3 Hz), 68.4 (u), 30.3 (u), 29.9 (u), 27.0 (dn), 22.0 (u), 14.3 (u), 10.7 (dn); IR (neat, cm^{-1}): 3399, 2965, 1651, 1511, 1221, 1021, 913 ; HRMS-EI m/z: [M+H], calc'd for $C_{12}H_{16}FO$, 195.1185; found 195.1190.

(1S,2R)-(+)-1-Ethyl-2-n-butyl-cyclopropylmethanol (10a)



General procedure was followed starting with **10** (22 mg, 0.097 mmol) and a 1.0 M diisobutylaluminium hydride solution (0.30 mL, 0.30 mmol) to give 12 mg (0.078 mmol, 80%) of **10a** as a colorless oil. The purity was measured to be > 95% by ^{1}H NMR. The enantiomeric excess of the major diastereomer was measured to be 72% ee and the minor diastereomer 65%ee by chiral GC analysis (G-TA column, 50-180°C, 2°C / min, flow rate 1 mL/min). A repetition of that experiment gave **10a** in 80% yield. We encountered difficulty in synthesizing racemic 10a. In order to observe the opposite enantioselectivity trend, we instead synthesized (1R,2S)-**10** using Rh_2(*R*-PTTL)$_3$(TPA) as catalyst, then followed the general procedure to make (1R,2S)-**10a**. The enantiomeric excess of the major diastereomer was measured to be -72%ee and the minor diastereomer -70%ee by

chiral GC analysis (G-TA column, 50-180 °C, 2°C / min, flow rate 1 mL/min). Spectral properties of the chromatographed material: $[\alpha]^{20}_{D}$ = -2.7° (c. 0.30 CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6 δ): 3.46-3.07 (m, 2H), 1.51-1.43 (m, 1H), 1.37-1.23 (m, 6H), 1.15-1.10 (m, 2H), 0.98-0.94 (m, 3H), 0.93-0.87 (m, 3H), 0.66 (s, 1H), 0.51-0.44 (m, 1H), 0.32 (td, J = 7.40, 4.04Hz, 1H), -0.19 (t, J = 4.91Hz, 1H) ; ^{13}C NMR (100 MHz, C_6D_6 δ) for the major diastereomer: 69.16 (u), 33.12 (u), 29.48 (u), 29.15 (u), 23.35 (u), 23.18 (dn), 22.47 (u), 16.19 (u), 14.76 (dn), 11.81 (dn) ^{13}C NMR (100 MHz, $CDCl_3$ δ) for the minor diastereomer: 64.22 (u), 33.19 (u), 29.51 (u), 27.82 (u), 24.77 (dn), 23.33 (u), 17.04 (u), 14.72 (dn), 11.26 (dn) ; IR (CH_2Cl_2, low concentration, cm^{-1}): 3690, 2986, 1424, 1265, 1170, 741; HRMS-EI (70 -VSE) m/z: [M^+], calc'd for $C_{10}H_{20}O$, 156.15142; found 156.15266.

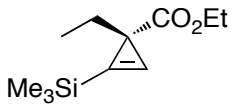
General procedure for cyclopropenation of aliphatic alkynes to provide nearly racemic products

In a dry round bottomed flask, Rh_2(*S*-PTTL)$_3$(TPA)/ Rh_2(*R*-PTTL)$_3$(TPA) (1:1) (0.0018 mmol) or Rh_2(*S*-PTTL)$_4$/ Rh_2(*R*-PTTL)$_4$ (1:1) (0.0018 mmol) and the appropriate alkyne (0.365 mmol) were dissolved in anhydrous toluene (3 mL) and cooled by a bath of dry ice/acetone (−78°C) under nitrogen atmosphere. The appropriate diazoester (1.10 mmol) was dissolved in anhydrous toluene (1 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. Upon completion of addition, the mixture was allowed to warm to room temperature. The solvent was subsequently removed, and the residue was chromatographed on silica gel deactivated with $EtSiCl_3$[10].

General procedure for enantioselective cyclopropenation of aliphatic alkynes

In a dry round bottomed flask, Rh_2(*S*-PTTL)$_3$(TPA) (2.3 mg, 0.0018 mmol) and the approptiate alkyne(0.365 mmol) were dissolved in anhydrous toluene (3 mL) and cooled by a bath of dry ice/acetone (−78 °C) under nitrogen atmosphere. The appropriate diazoester (1.10 mmol) was dissolved in anhydrous toluene (1.05 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. After the addition was complete, the mixture was allowed to warm to room temperature. The solvent was subsequently removed and the residue was chromatographed on silica gel deactivated with $EtSiCl_3$[10].

(R)-(−)-Ethyl 1-ethyl-2-(trimethylsilyl)cyclopropene-1-carboxylate (11)

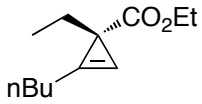


The general procedure for enantioselective cyclopropenation was followed with ethyl 2-diazo butanoate (217 mg, 1.53 mmol) and (30 mg, 0.31 mmol) of 1-hexyne to give 53 mg (0.25 mmol, 82%) of the title compound as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. The enantiomeric excess of the title compound was measured by GC (CHIRALDEX G-TA) to be 91% ee. A repetition of that experiment gave **11** in 81% yield. Note: It is very important that the diazoester contain no trace impurities whatsoever. We found that, when using diazoester made from diazo transfer with p-acetamidobenzene sulfonyl azide, yields were much lower. This was attributed to a very small trace impurtity present in the diazoester (< 1%) observed by NMR. When using diazoester made from diazo transfer with tosyl azide, which we were able to isolate with no trace impurities, the reaction proceeded in good yield as reported above.

Spectral properties of the chromatographed material: $[\alpha]^{20}_D$ = -31.° (c. 0.064 $CHCl_3$); ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 4.06 (m, 2H), 2.01 – 1.89 (m, 1H), 1.70 – 1.60 (m, 1H), 1.20 (t, J = 7.1 Hz, 3H), 0.71 (t, J=7.5 Hz, 3H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7(u), 119.5(u), 119.1(u), 60.3(u), 28.8(u), 26.5(u), 14.6(dn), 11.7(dn), -1.1(dn). IR (neat, cm^{-1}):2961, 1720, 1694, 1456, 1250, 1126, 1040, 843, 757, 710, 698; HRMS-EI (70 -VSE) m/z: [M^+], calc'd for $C_{11}H_{20}O_2Si$, 212.12326 ; found 212.12404.

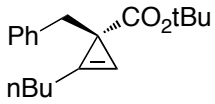
(R)-(−)-Ethyl 1-ethyl-2-(n-butyl)cyclopropene-1-carboxylate (12)



The general procedure for enantioselective cyclopropenation was followed with ethyl 2-diazobutanoate with (156 mg, 1.10 mmol) and 1-hexyne (30 mg, 0.37 mmol) to give 62 mg (0.314 mmol, 86%) of the title compound as a colorless oil. The enantiomeric excess of the title compound was measured by GC (CHIRALDEX G-TA) to be 72% ee. A repetition of that experiment gave **12** in 85% yield. Spectral properties of the chromatographed material: $[\alpha]^{20}_D$ = -30° (c. 0.061 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.41 (s, 1H), 4.15 – 4.00 (m, 2H), 2.49 – 2.42 (m, 2H), 1.99-1.87 (m, 1H), 1.72-1.61 (m, 1H), 1.61 – 1.49 (m, 2H), 1.45 – 1.32 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H), 0.94 – 0.87 (m, 3H), 0.75 (t, J = 7.5 Hz, 3H). Inseparable impurities were observed at 4.18, 1.28-1.24, and 1.03-0.98ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5(u), 120.5(u), 98.3(u), 60.3(u), 30.3(u), 29.2(u), 25.5(u), 24.7(u), 22.4(u), 14.5(dn), 13.9(dn), 11.5(dn). IR (neat, cm^-

[1]):2960, 2933, 2873, 1715, 1461, 1366, 1235, 1126, 1038, 749; HRMS-EI (70 -VSE) m/z: [M^+], calc'd for $C_{12}H_{20}O_2$, 196.14633 ; found 196.14547.

(R)-(−)-*tert*-Butyl 1-ethyl-2-benzylcyclopropene-1-carboxylate (13)

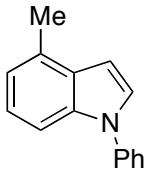


The general procedure for enantioselective cyclopropenation was followed with *tert*-butyl 2-diazo-3-phenylproprionate (166 mg, 0.714 mmol) and 1-hexyne (20 mg, 0.24 mmol) to give 62 mg (0.16 mmol, 68%) of the title compound as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and HPLC. The enantiomeric excess of the title compound was measured to be 94% ee HPLC analysis (CHIRACEL IB column, 0.1% isopropanol in hexanes, 1 mL/min, 220 nm). A repetition of that experiment gave **13** in 67% yield. Spectral properties of the chromatographed material: $[\alpha]^{20}_D$ = +18° (c. 0.067 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.18 – 7.14 (m, 1H), 7.14 – 7.08 (m, 2H), 6.31 (s, 1H), 3.23 (d, J = 14.4 Hz, 1H), 2.94 (d, J = 14.4 Hz, 1H), 2.41 – 2.26 (m, 2H), 1.52 – 1.42 (m, 2H), 1.39 (s, 9H), 1.37 – 1.29 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4(u), 140.8(u), 129.4(dn), 128.2(dn), 125.8(dn), 120.1(u), 100.2(u), 98.8(u), 79.9(u), 39.7(u), 31.2(u), 29.2(u), 28.3(dn), 24.5(u), 22.4(u), 14.0(dn). IR (neat, cm^{-1}): 3444.4, 3020.6, 1638.4, 1523.1, 1425.5, 1215.7, 1046.6, 927.6, 770.5; HRMS-EI (70 -VSE) m/z: [M^+], calc'd for $C_{19}H_{26}O_2$, 287.14360 ; found 287.14450

General procedure for indole C-H insertion to provide racemic products

In a dry round bottomed flask, Rh_2Piv_4 (0.295 mg, 0.00483 mmol)) and the appropriate indole (0.0965 mmol) were dissolved in anhydrous toluene (0.72 mL) and cooled by a bath of dry ice/acetone (−78°C) under nitrogen atmosphere. The appropriate diazoester (0.483 mmol) was dissolved in anhydrous toluene (0.250 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. Upon completion of addition, the mixture was allowed to warm to room temperature. The solvent was subsequently removed, and the residue was chromatographed on silica gel.

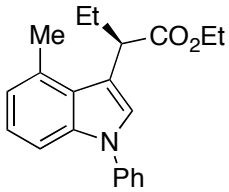
4-Methyl-1-phenylindole (14)



A literature precedent was followed.[9] Thus, a resealable Schlenk tube was charged with CuI (78 mg, 0.41 mmol), 4-methylindole (1.07 g, 8.17 mmol), and K_3PO_4 (3.64 g, 17.2 mmol) and the vessel was evacuated and filled with N_2. Iodobenzene (1.1 mL, 9.8 mmol), *N*,*N*'-dimethylethylenediamine (0.18 mL, 1.63 mmol), and toluene (8.2 mL) were then added and the vessel was sealed and heated to 110 °C for 24 h. The reaction mixture was then allowed to cool to ambient temperature, diluted with 50 mL of ethyl acetate, filtered through a plug of silica eluting with 200 mL of additional ethyl acetate, concentrated, and chromatographed on silica gel eluting with a gradient of 0 – 3% ethyl acetate/hexanes to give 1.45 g (7.00 mmol, 86%) of **14**. Spectral properties of the chromatographed material: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 4H), 7.46 – 7.30 (m, 3H), 7.18 –

7.10 (m, 1H), 6.99 (d, J = 7.0 Hz, 1H), 6.72 (d, J = 3.2 Hz, 1H), 2.61 (d, J = 7.2 Hz, 3H), 1.54 (s, 1H), 1.43 (s, 1H), 1.27 (dd, J = 22.8, 10.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.10(u), 135.66(u), 130.72(u), 129.72(dn), 129.21(u), 127.49(dn), 126.54(dn), 124.52(dn), 122.61(dn), 120.65(dn), 108.28(dn), 102.12(dn), 18.92(dn). IR (CH_2Cl_2, cm^{-1}): 3049, 2974, 2922, 2858, 1597, 1501, 1456, 1427, 1323, 1266, 1213, 1161, 1074, 1030, 922, 752 ; HRMS-EI (70 -VSE) m/z: [M^+], calc'd for $C_{15}H_{13}N$, 207.10480; found 207.10539.

(*R*)-ethyl 2-(4-methyl-1-phenyl-indol-3-yl)butanoate (15)



In a dry round bottomed flask, Rh_2(*S*-PTTL)$_3$(TPA) (1.53 mg, 0.00121 mmol) and 4-methyl-1-phenyl-indole **14** (50 mg, 0.15 mmol) were dissolved in anhydrous toluene (1.8 mL) and cooled by a bath of dry ice/acetone (−78 °C) under nitrogen atmosphere. Ethyl-2-diazobutanoate (343 mg, 2.41 mmol) was dissolved in anhydrous toluene (0.600 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. After the addition was complete, the mixture was allowed to warm to room temperature. The solvent was subsequently removed under vacuum, and the residue was chromatographed on silica gel deactivated with $EtSiCl_3$[10]. to give 62 mg (0.19 mmol, 80%) of the title compound as a pale yellow oil. Enantiomeric excess of the title compound was measured by HPLC

(CHIRACEL IB, 0.25% isopropyl alcohol/hexanes) to be 81% ee. A repetition of that experiment gave **15** in 79% yield. Spectral properties of the chromatographed material: $[\alpha]^{20}_{D}$ = -32° (c. 0.047 $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.47 (s, 1H), 7.36 (d, J = 8.6 Hz, 1H), 7.13-6.92 (m, 7H), 4.37 (dd, J = 9.1, 6.3 Hz, 1H), 4.08-3.89 (m, 2H), 2.81 (s, 3H), 2.37-2.21 (m, 1H), 2.06-1.93 (m, 1H), 1.04 (t, J = 7.3 Hz, 3H), 0.92 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 175.1(u), 140.4(u), 137.3(u), 131.3(u), 129.4(dn), 127.7(u), 126.7(dn), 126.4(dn), 125.3(dn), 123.3(dn), 123.2(dn), 117.4(u), 109.6(dn), 60.9(u), 45.7(dn), 29.2(u), 21.4(dn), 14.5(dn), 13.1(dn). IR (neat, cm^{-1}):2966, 2932, 1733, 1595, 1501, 1460, 1425, 1261, 1227, 1156, 1115, 1024, 752, 699; HRMS-EI (70 -VSE) m/z: [M^+], calc'd for $C_{21}H_{23}O_2N$, 321.17288; found 321.17226.

Computational details:

For the conformational search, the Molecular Operating Environment (MOE), version 2010.10[12], was employed using LowModMD method[13] and MMFF94x force-field. 14 Atoms (two Rh atoms, 8 Oxygens and 4 neighboring carbons) were fixed. Energy window, Iteration limit and MM Iteration limit were set to to 5 kcal/mol, 1000 and 500, respectively. The other LowModMD options were kept default. Eight conformers were located and subjected to further QM re-optimization at the B3LYP/lanl2dz level of theory using Gaussian g09.[14]

Cartesian coordinates of lowest energy conformer [Figure 1(c)] (fully optimizized at the RB3LYP/LANL2DZ). Electronic Energy: -3833.14120165 a.u.

Rh	0.05098	-0.11209	0.48980
Rh	0.64966	-0.38156	-1.83092
N	-0.44655	-4.73357	0.82052

N	-4.49960	-0.18196	-0.76965
N	-0.65004	4.53917	-0.10455
O	2.04949	0.20926	0.90022
O	2.60938	-0.03770	-1.29965
O	0.33998	-2.13810	0.73141
O	0.92950	-2.40522	-1.46744
O	-2.15119	-3.70288	-0.45110
O	0.73905	-5.70604	2.62027
O	-1.90424	-0.48898	-0.04428
O	-1.33153	-0.77622	-2.24653
O	-3.47801	1.84980	-1.40901
O	-5.70973	-1.79473	0.46706
O	-0.28306	1.88613	0.12964
O	0.25522	1.63293	-2.08344
O	-2.95332	5.05644	0.08038
O	1.65445	4.31549	0.40244
C	2.93257	0.12124	-0.05173
C	4.44255	0.12026	0.34754
C	4.02610	2.33810	1.58125
C	4.28698	3.24705	2.61911
C	5.18696	2.91557	3.65068
C	5.82186	1.66101	3.62821
C	5.56029	0.75138	2.58554

C	4.65742	1.07475	1.55240
C	5.28479	-0.19622	-2.07033
C	6.06172	0.17531	-3.17726
C	6.88927	1.31466	-3.11729
C	6.92640	2.06833	-1.93307
C	6.14207	1.69363	-0.82318
C	5.30463	0.56036	-0.87293
C	5.96868	-1.98351	0.39981
C	6.27525	-3.28641	0.83729
C	5.37611	-3.99302	1.65585
C	4.17332	-3.37329	2.04626
C	3.87443	-2.06784	1.61784
C	4.75867	-1.35872	0.77058
C	0.65880	-2.87662	-0.29254
C	0.73489	-4.39187	-0.00134
C	1.01294	-5.36256	-1.20444
C	2.43050	-5.05228	-1.76003
C	-0.03365	-5.25530	-2.34053
C	1.01199	-6.81266	-0.64699
C	-1.77403	-4.30647	0.57108
C	-2.57200	-4.70175	1.76668
C	-3.92608	-4.50080	2.04440
C	-4.40486	-4.97627	3.28753

C	-3.54437	-5.61732	4.20584
C	-2.17124	-5.79616	3.91746
C	-1.70813	-5.32671	2.68721
C	-0.32918	-5.31914	2.11245
C	-2.19766	-0.75797	-1.28431
C	-3.66973	-1.12440	-1.54680
C	-4.13012	-1.32807	-3.03572
C	-3.37905	-2.55763	-3.61810
C	-5.64955	-1.65347	-3.01684
C	-3.88802	-0.09027	-3.93437
C	-4.31449	1.22397	-0.73158
C	-5.28164	1.74032	0.28032
C	-5.53157	3.05062	0.69335
C	-6.51880	3.23327	1.68997
C	-7.20977	2.13444	2.24616
C	-6.93354	0.81184	1.82780
C	-5.96332	0.64109	0.83904
C	-5.43494	-0.60665	0.20750
C	-0.18680	2.33633	-1.08604
C	-0.74640	3.74762	-1.34808
C	-0.25710	4.49375	-2.65084
C	1.28251	4.49752	-2.82298
C	-0.77079	5.95807	-2.58736

C	-0.91854	3.80502	-3.87773
C	-1.78973	5.10374	0.52309
C	-1.30160	5.73805	1.78370
C	-1.99735	6.44653	2.76509
C	-1.25704	6.92849	3.86858
C	0.13267	6.69721	3.96765
C	0.82429	5.97827	2.96624
C	0.08246	5.50939	1.88082
C	0.51522	4.72905	0.68102
H	3.32598	2.63174	0.80518
H	3.78857	4.21288	2.60836
H	5.38910	3.61992	4.45479
H	6.51993	1.38716	4.41618
H	6.06274	-0.21052	2.58668
H	4.65616	-1.07707	-2.13840
H	6.02123	-0.42275	-4.08484
H	7.49177	1.60432	-3.97529
H	7.56101	2.94900	-1.86456
H	6.19331	2.29497	0.07688
H	6.67908	-1.45943	-0.23004
H	7.21620	-3.74254	0.53788
H	5.60926	-5.00117	1.99030
H	3.47219	-3.89871	2.69112

H	2.95752	-1.59802	1.95682
H	1.58554	-4.50655	0.68771
H	2.68811	-5.78705	-2.53378
H	2.47490	-4.05485	-2.20571
H	3.19411	-5.11532	-0.97197
H	0.22897	-5.96254	-3.13898
H	-1.04151	-5.50268	-1.98953
H	-0.06123	-4.24853	-2.76602
H	1.31374	-7.50852	-1.43989
H	0.01502	-7.11298	-0.30140
H	1.71107	-6.92594	0.19141
H	-4.57679	-3.98022	1.34664
H	-5.45188	-4.83893	3.54436
H	-3.94418	-5.96916	5.15345
H	-1.49847	-6.27191	4.62474
H	-3.79242	-2.09478	-1.04562
H	-3.77551	-2.78575	-4.61631
H	-3.51475	-3.44484	-2.98590
H	-2.30710	-2.36456	-3.70703
H	-5.98065	-1.90520	-4.03237
H	-6.24565	-0.79800	-2.67524
H	-5.87231	-2.50735	-2.36419
H	-4.22220	-0.31659	-4.95617

H	-4.44630	0.78492	-3.58397
H	-2.82791	0.17619	-3.96891
H	-4.97330	3.88453	0.27754
H	-6.74772	4.23710	2.03853
H	-7.96152	2.30989	3.01161
H	-7.45183	-0.04040	2.25713
H	-1.82703	3.57299	-1.47637
H	1.54166	5.06066	-3.72990
H	1.67290	3.48098	-2.93252
H	1.79029	4.96497	-1.97333
H	-1.85264	6.00016	-2.40612
H	-0.56946	6.45399	-3.54525
H	-0.26620	6.53551	-1.80268
H	-2.01434	3.82295	-3.80005
H	-0.63518	4.33962	-4.79395
H	-0.59686	2.76486	-3.97124
H	-3.06620	6.61794	2.67951
H	-1.76168	7.48438	4.65451
H	0.67578	7.07729	4.82895
H	1.89172	5.79382	3.03641

Cartesian coordinates of next lowest energy conformer [Footnote 14] (molecular dynamics/ fully optimizized at the RB3LYP/LANL2DZ). Higher in energy than lowest energy conformer by +0.5 kcal/mol.

Rh	-0.13029	-0.17653	0.51830
Rh	0.10815	-0.75390	-1.81227
N	-3.70741	-3.12236	0.81817
N	-3.41806	2.96180	-0.63983
N	2.72851	3.59768	-0.14199
O	1.54321	-1.30803	0.92241
O	1.82918	-1.77576	-1.30092
O	-1.34097	-1.83298	0.72866
O	-1.06388	-2.43055	-1.46595
O	-4.19446	-1.13434	-0.36266
O	-3.56689	-4.74318	2.53412
O	-1.78759	0.92534	0.00223
O	-1.63061	0.30622	-2.19927
O	-5.38466	2.61515	0.62879
O	-1.28146	3.72165	-1.30112
O	1.01671	1.50550	0.16549
O	1.16617	1.00065	-2.06500
O	1.55588	5.57011	0.43935
O	4.15804	1.71725	-0.02318
C	2.18368	-1.87914	-0.05284
C	3.35073	-2.84154	0.29471
C	2.51519	-5.02382	-0.83525
H	3.04002	-4.73493	-1.73965

C	1.75850	-6.20904	-0.82477
H	1.72393	-6.83061	-1.71651
C	1.03763	-6.58340	0.32451
H	0.45547	-7.50222	0.33332
C	1.06559	-5.74838	1.45797
H	0.49306	-6.00987	2.34463
C	1.82951	-4.56881	1.44762
H	1.82621	-3.92455	2.32169
C	2.58705	-4.20463	0.31124
C	4.22946	-1.15786	2.04063
H	3.85419	-0.34501	1.42843
C	4.93594	-0.85186	3.21586
H	5.07340	0.18900	3.50047
C	5.46005	-1.87723	4.02514
H	6.00643	-1.63814	4.93481
C	5.27224	-3.21643	3.63811
H	5.67935	-4.02297	4.24383
C	4.55862	-3.52116	2.46556
H	4.42745	-4.56259	2.18711
C	4.01444	-2.49943	1.65781
C	4.77869	-1.58137	-1.45650
H	4.13522	-0.71357	-1.36085
C	5.90006	-1.49713	-2.30068

H	6.09247	-0.57176	-2.83859
C	6.77057	-2.59259	-2.44568
H	7.63688	-2.52513	-3.09978
C	6.51127	-3.77390	-1.72486
H	7.18114	-4.62636	-1.81297
C	5.39041	-3.85597	-0.88233
H	5.21855	-4.77119	-0.32268
C	4.49824	-2.76898	-0.74827
C	-1.61850	-2.57368	-0.30425
C	-2.65592	-3.69238	-0.05149
H	-2.14087	-4.42435	0.58979
C	-3.19179	-4.49495	-1.29406
C	-4.26086	-5.49876	-0.78077
H	-4.56370	-6.15909	-1.60314
H	-5.15942	-4.98461	-0.41808
H	-3.87366	-6.12376	0.03400
C	-2.01161	-5.30528	-1.89543
H	-1.22759	-4.64809	-2.28090
H	-2.37977	-5.92630	-2.72250
H	-1.56395	-5.97321	-1.14721
C	-3.82404	-3.59833	-2.38680
H	-4.67642	-3.02797	-2.00307
H	-4.18380	-4.23387	-3.20743

H	-3.09817	-2.88890	-2.79381
C	-4.33918	-1.86915	0.63259
C	-5.16236	-1.63029	1.85234
C	-5.96730	-0.53929	2.18856
H	-6.06523	0.31792	1.52746
C	-6.62484	-0.58737	3.43998
H	-7.25984	0.24139	3.74189
C	-6.46409	-1.68915	4.30895
H	-6.98229	-1.69339	5.26451
C	-5.63254	-2.77885	3.96028
H	-5.49038	-3.62314	4.62822
C	-4.98993	-2.72438	2.72229
C	-4.03173	-3.67923	2.08760
C	-2.20921	0.93975	-1.22927
C	-3.50768	1.73598	-1.46182
H	-4.27902	1.12363	-0.97402
C	-3.98758	1.96672	-2.93985
C	-2.93731	2.67051	-3.83392
H	-3.34581	2.78256	-4.84762
H	-2.01373	2.08791	-3.89774
H	-2.68366	3.66833	-3.45971
C	-4.35790	0.58736	-3.55300
H	-5.09584	0.06060	-2.93360

H	-3.47809	-0.05341	-3.65332
H	-4.79402	0.73736	-4.54950
C	-5.27452	2.83563	-2.88511
H	-5.69692	2.92458	-3.89393
H	-5.06571	3.84924	-2.52058
H	-6.03748	2.38861	-2.23470
C	-4.35362	3.27038	0.38178
C	-3.82026	4.48201	1.07660
C	-4.34934	5.22607	2.13238
H	-5.31053	4.97334	2.56998
C	-3.58152	6.31381	2.61020
H	-3.96007	6.91919	3.42992
C	-2.32335	6.62087	2.04709
H	-1.75048	7.45405	2.44579
C	-1.79213	5.85824	0.98065
H	-0.81102	6.06533	0.56233
C	-2.57171	4.80059	0.50767
C	-2.29276	3.82046	-0.58056
C	1.35124	1.79544	-1.05816
C	1.89592	3.21570	-1.29911
H	0.99824	3.84819	-1.22212
C	2.54069	3.52879	-2.70326
C	3.66785	2.54563	-3.10679

H	3.29070	1.52171	-3.18637
H	4.49439	2.55053	-2.38819
H	4.06750	2.84124	-4.08649
C	3.11707	4.97082	-2.65079
H	3.45210	5.26325	-3.65387
H	3.98177	5.04332	-1.97899
H	2.36266	5.69659	-2.32109
C	1.41473	3.50088	-3.77481
H	0.60097	4.19110	-3.51653
H	0.99097	2.49945	-3.88287
H	1.82845	3.80834	-4.74438
C	2.46786	4.74711	0.64641
C	3.48821	4.73862	1.73861
C	3.71493	5.65218	2.76939
H	3.10066	6.54146	2.87414
C	4.77319	5.37425	3.66513
H	4.98312	6.06203	4.48008
C	5.56561	4.21464	3.51728
H	6.37387	4.02880	4.21976
C	5.32294	3.29486	2.47128
H	5.92945	2.40271	2.34527
C	4.27595	3.58153	1.59374
C	3.77528	2.82004	0.40979

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