Supporting Information

Highly enantioselective intermolecular carbene insertion to C-H and Si-H bonds catalyzed by a chiral iridium(III) complex of D_4-Symmetric Halterman porphyrin ligand

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Content

General Methods

Reagents were obtained commercially and used without further purification unless indicated otherwise. All anhydrous solvents used in the reactions were dried and freshly distilled. NMR spectra were recorded in $CDCl_3$ on a Bruker AM300 spectrometer at 25 ºC with TMS as an internal standard. Mass spectra were obtained on a HP5989A spectrometer (EI), an IonSpec 4.7 Tesla FTMS spectrometer (MALDI), or a Bruker Daltonics FTMS-7 spectrometer (ESI). Optical rotations were measured on a Perkin-Elmer 341MC polarimeter. IR spectra were recorded, using KBr discs, on a Bio-Rad FTS-185 machine. X-ray diffraction data were collected on Bruker SMART APEX CCD with graphite monochromatized MoKα radiation. All the α-substituted α-diazoacetates were also prepared according to the reported procedures.[1]

Synthesis of iridium porphyrin complexes 1 and 2

Porphyrins were prepared according to the reported method.[2]

Complexes **1** and **2** were prepared according to the method as follows: A mixture of porphyrin ligand (0.2 mmol) and $[Ir(cod)Cl_2]_2$ (1.5-2 eq.) in 1,2,4-trichlorobenzene (20 mL) was heated to 190°C until the porphyrin ligand disappeared (monitored by TLC), then the mixture was purified by silica gel column and [Ir(por)(CO)Cl] was obtained as a red powder solid. This red solid was treated with $NaBH_4$ and MeI to afford the complex **1** or **2**[3]

[Ir(TTP)(CO)Cl] (yield: 68%)

^{1}H NMR(300 MHz, $CDCl_3$): δ 8.94 (s, 8H), 8.16 (d, J = 7.2 Hz, 4H), 8.09 (d, J = 7.2 Hz, 4H), 7.57 (d, J = 7.2 Hz, 8H), 2.71 (s, 12H);

^{13}C NMR(75 MHz, $CDCl_3$): 141.25, 138.40, 137.78, 135.04, 134.53, 134.27, 131.88, 127.78, 127.52, 122.20, 21.62;

IR(KBr): 2058, 2045, 1358, 1179, 1074, 1025, 1018, 797, 713 cm^{-1};

MS(MALDI) m/z(relative intensity): 863[M-CO-Cl], 898[M-CO]

HRMS(MALDI) For $[C_{49}H_{36}N_4OCl^{191}Ir^+]$: Calcd. 922.21781; Found: 922.2164 ± 0.004;

Element analyses calcd for: C: 63.66%, H: 3.92%; Found C: 64.05%, H: 4.42%.

UV-Vis(λa)([C] ≈ 2*10^{-6}M): 421nm ;

[Ir(TTP)Me] (yield : 70%)

^{1}H NMR(300 MHz, $CDCl_3$): δ 8.51 (s, 8H), 8.01 (t, J = 8.4 Hz, 8H), 7.51 (d, J = 7.8 Hz, 8H), 2.68 (s, 12H), -6.30(s, 3H);

MS(MALDI) m/z: 877[M], 862[M-15];

HRMS(MALDI)For $C_{49}H_{39}N_4{}^{191}Ir^+$: Calcd.874.27751; Found.874.2771 ± 0.004;

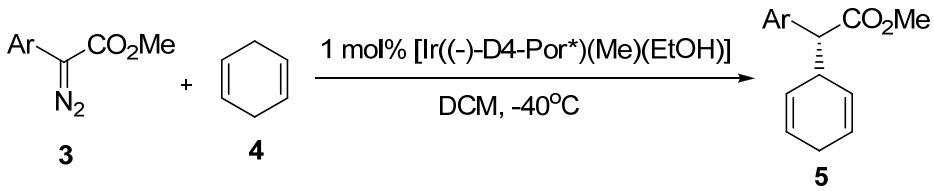
IR(KBr): 3022, 2918, 1354, 1308, 1071, 1012, 799, 720 cm^{-1};

[Ir((-)-D*$_4$-por)(CO)Cl] (yield: 83%)

^{1}H NMR(300 MHz, $CDCl_3$): δ 8.75 (s, 8H), 7.38 (s, 4H), 3.59 (br, 4H), 3.54 (s, 4H), 2.77 (s, 4H), 2.71 (s, 4H), 2.03-1.85 (m, 16H), 1.45-1.07 (m, 32H);

IR(KBr): 2962, 2870, 2047, 1447, 1297, 1107, 797, 705 cm^{-1};
MS(MALDI) m/z: 1334[M-CO-Cl], 1370[M-CO];
HRMS (MALDI) For $C_{85}H_{76}N_4OCl^{191}Ir^+$: Calcd.1394.5308; Found.1394.5340 ±0.005;
UV-Vis(λa)([C] ≈ $2*10^{-6}$M): 423 nm;
[Ir((-)-D*$_4$-por)Me] (yield: 80%)
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, *J* = 3.9 Hz, 4H), 8.34 (d, *J* = 3.9 Hz, 4H), 7.33 (s, 4H), 3.55 (br, 8H), 2.82 (s, 4H), 2.78 (s, 4H), 1.99-1.97 (m, 8H), 1.91-1.85(m, 1H), 1.42-1.37(m, 24H), 1.19-1.13(m, 8H)-6.11(s, 3H);
MS(MALDI) m/z: 1349[M], 1334[M-15];
HRMS(MALDI) For $C_{85}H_{79}N_4{}^{191}Ir^+$: Calcd: 1346.59051; Found: 1346.5919 ± 0.005;
IR(KBr): 2960, 2919, 2868, 1298, 1106, 1016, 796, 710 cm^{-1};

Procedure for asymmetric C-H bond insertion of cyclohexa-1,4-diene with methyl aryldiazoacetate catalyzed by [Ir((-)-D$_4$-Por*)(Me)(EtOH)] 2



To a solution of **3** (0.4 mmol) and cyclohexa-1,4-diene (4 mmol) in anhydrous dichloromethane (4 mL), after stirring 10 minutes at -40°C catalyst **2** (1 mol%) was added. The reaction was stirred for 24 hours at -40°C and then purified by chromatography on a silica gel column with dichloromethane/petroleum ether (1:5) as eluent to yield the product **5a-5g**.

5a (*R*)-methyl 2-(cyclohexa-2,5-dienyl)-2-phenylacetate; 90%, HPLC (OJ-H, 100:1 hexane/2-propanol, 0.7 mL/min, 214 nm) retention times of 11.6 min (major) and 13.6 min (minor), 95%ee; $[\alpha]_D^{28}$ -58.4(*c* = 1.0, $CHCl_3$); Lit.[4][94% ee; $[\alpha]_D^{21}$ -108.8(*c* = 1.1, $CHCl_3$)];
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.34-7.27 (m, 5H), 5.83-5.66 (m, 3H), 5.28-5.23 (m, 1H), 3.68 (s, 3H), 3.48-3.40 (m, 2H), 2.63-2.59 (m, 2H);
MS(EI) m/z(relative intensity): 226(M-2, 17), 167(100), 77(87), 105(87), 150(81), 118(53), 79(50), 107(42), 165(42);
IR(film): 3030, 1736, 1454, 1435, 1273, 1159, 735, 698cm^{-1};

5b (*R*)-(methyl 2-(cyclohexa-2,5-dienyl)-2-(4-methoxyphenyl)acetate); 94%, HPLC (Sino-AD, 98:2/hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 9.9 min (major) and 10.5 min (minor), 96% ee; $[\alpha]_D^{28}$ -126.7(*c* = 1.0, $CHCl_3$); Lit.[4][90% ee; $[\alpha]_D^{21}$ -126.1(*c* = 1.18, $CHCl_3$)];
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.25 (d, *J* = 9.0Hz, 2H), 6.85 (d, *J* = 9.0Hz, 2H), 5.81-5.66 (m, 3H), 5.30-5.26 (m, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 3.43-3.34 (m, 2H), 2.62-2.59 (m, 2H);

MS(EI) m/z(relative intensity): 180(100), 165(61), 121(54), 77(27), 148(25), 151(22), 79(18), 135(18);
IR(film): 3030, 1733, 1610, 1512, 1251, 1179, 1157, 1035, 829cm^{-1};
5c (*R*)-(methyl 2-(4-bromophenyl)-2-(cyclohexa-2,5-dienyl)acetate); 91%, HPLC (AD-H, 98:2/hexane:2-propanol; 0.7 mL/min, 214 nm) retention times of 8.3 min (major) and 8.8 min (minor), 96% ee; $[\alpha]_D^{28}$ -72.7(*c* = 1.0, $CDCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.1Hz, 2H), 7.21 (d, *J* = 8.1Hz, 2H,), 5.82-5.65 (m, 3H), 5.29-5.25 (m, 1H), 3.68 (s, 3H), 3.45-3.38 (m, 2H), 2.60-2.57 (m, 2H);
MS(EI) m/z(relative intensity): 228(100), 230(98), 79(70), 77(57), 196(36), 198(35), 134(32), 89(31);
IR(film): 3029, 1736, 1488, 1269, 1192, 1159, 1103, 1012cm^{-1};

5d (*R*)-methyl 2-(4-chlorophenyl)-2-(cyclohexa-2,5-dienyl)acetate; 82%, colorless oil, HPLC (OD-H, 200:1/hexane:2-propanol, 0.9 mL/min, 214 nm) retention times of 13.6 min (minor) and 21.4 min (major), 98% ee; $[\alpha]_D^{20}$ -129.1 (*c* = 1.2, $CDCl_3$); Lit.[4][95% ee; $[\alpha]_D^{21}$ -138.5(*c* = 1.52, $CHCl_3$)];
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.31-7.25(m, 4H), 5.83-5.66(m, 3H), 5.29-5.25(m, 1H), 3.69(s, 3H), 3.47-3.39(m, 2H), 2.61-2.59(m, 2H);
MS(EI) m/z(relative intensity): 260(3), 184(100), 79(48), 77(46), 152(44), 186(29), 139(28), 165(27);
IR(neat): 3445, 3031, 1736, 1491, 1269, 1158, 1091, 1016, 700 cm^{-1};

5e (*R*)-methyl 2-(3-chlorophenyl)-2-(cyclohexa-2,5-dienyl)acetate; 90%, HPLC (Sino-AD, 98:2/hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 6.6 min (major) and 7.1 min (minor), 86% ee; $[\alpha]_D^{28}$ -72.7 (*c* = 1.0, $CDCl_3$); Lit.[4][99% ee; $[\alpha]_D^{21}$ -158.6(*c* = 0.39, $CHCl_3$)];
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.43-7.40 (m, 1H), 7.25-7.23 (m, 3H), 5.84-5.66 (m, 3H), 5.29-5.24 (m, 1H), 3.70 (s, 3H), 3.48-3.38 (m, 2H), 2.62-2.60 (m, 2H);
MS(EI) m/z(relative intensity): 262(10), 201 (100), 165(93), 184(68), 166(63), 152(61), 139(44), 77(42), 79(40);
IR(film): 3031, 1736, 1477, 1433, 1267, 1192, 1159, 692, 681cm^{-1};

5f (*R*) –(methyl 2-(naphthalen-2-yl)-2-(cyclohexa-2,5-dienyl)acetate); 85%, colorless oil, HPLC (IC, 95:5/hexane:2-propanol, 0.4 mL/min, 214 nm) retention times of 11.7 min (minor) and 12.2 min(major), 95% ee; $[\alpha]_D^{20}$ -121.1 (c = 1.0, $CDCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.83-7.78 (m, 4H), 7.52-7.45 (m, 3H), 5.85-5.65 (m, 3H), 5.28-5.25 (m, 1H), 3.68 (s, 3H), 3.60 (br, 2H), 2.62 (br, 2H);
MS(EI) m/z(relative intensity): 276(21), 200(100), 217(93), 168(84), 141(62), 155(50), 215(44), 202(41);
IR(neat): 3440, 3025, 1730, 1507, 1235, 1159, 1016, 814, 752, 697 cm^{-1};

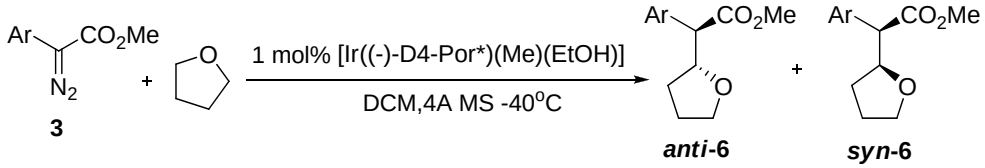
5g (*R*)-(methyl 2-(thiophen-3-yl)-2-(cyclohexa-2,5-dienyl)acetate); 62%, colorless oil, HPLC (OB-H, 100:1/hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 22.0

min (major) and 24.7 min (minor), 96% ee; $[\alpha]_D^{20}$ -69.2 (c = 1.0, $CDCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.36-7.09 (m, 3H), 5.82-5.63 (m, 3H), 5.40-5.35 (m, 1H), 3.63 (s, 3H), 3.60-3.40 (m, 2H), 2.62-2.59 (m, 2H);
MS(EI) m/z(relative intensity): 232(M, 1), 173(100), 111(46), 129(20), 45(19), 171(16), 113(14), 174(13);
IR(neat): 3445, 3107, 1737, 1497, 1436, 1224, 1163, 1081, 1013, 770, 703 cm^{-1};

Procedure of the gram-scale reaction

In a oven dried Schlenk tube, the catalyst (0.01 mol%) and cyclohexa-1,4-diene (2 mL) was added. The red solution was stirred at 0°c for 20 minutes, then diazo compound (1.96 g) in cyclohexa-1,4-diene (1 mL) was added by syringe pump for 1 hour followed by stirring at 0°C until color of solution became red. Then the reaction mixture was filtrated and evaporated to afford the product. Yield: 96%, ee: 96%.

Procedure for asymmetric C-H bond insertion of THF with methyl aryldiazoacetate catalyzed by [Ir((-)-D_4-Por*)(Me)(EtOH)] 2



To a solution of **3** (0.4 mmol) and THF (4 mmol) and 4Å MS (160 mg) in anhydrous dichloromethane (4 mL), after stirring 10 minutes at -40°C catalyst **2** (1 mol%) was added. The reaction was stirred for 24 hours at -40°C ; the *anti*/*syn* ratio was determined by analysis of the crude reaction mixture with ^{1}H NMR spectroscopy. Further purification of the mixture by chromatography on a silica gel column with ethyl acetate/petroleum ether (1:10) as eluent to give the major product ***anti*-6 (6a-6h)**.

6a Methyl 2-phenyl-2-(tetrahydrofuran-2-yl)acetate; 82%, colorless oil, dr=10:1, HPLC (OD-H, 99:1/hexane:2-propanol, 0.7 mL/min, 250 nm) retention times of 21.8 min (major) and 23.6 min (minor), 90% ee; $[\alpha]_D^{28}$ -37.3 (*c* = 0.2, $CDCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.37-7.26 (m, 5H), 4.57-4.49 (m, 1H), 3.96-3.80 (m, 2H), 3.71 (s, 1H), 3.54 (d, *J* = 10.2Hz, 1H), 1.93-1.78 (m, 2H), 1.75-1.64 (m, 1H), 1.49-1.37 (s, 1H);
MS(EI) m/z(relative intensity): 220(M, 0.7), 71(100), 150(36), 43(25), 91(22), 176(18), 118(14), 77(9), 90(8);
IR(neat): 2951, 1739, 1455, 1434, 1205, 1160, 1111, 1067, 701cm^{-1};

6b Methyl 2-(4-bromophenyl)-2-tetrahydrofuran-2-yl)acetate; 96%, colorless oil, dr >20:1, HPLC (OB-H, 98:2/hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 19.5 min (minor) and 23.6 min (major), 97% ee; $[\alpha]_D^{20}$ -42.8(c = 1.2, $CDCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.7Hz, 2H), 7.24 (d, *J* = 8.7Hz, 2H), 4.50-4.43 (m, 1H), 3.95-3.82 (m, 2H), 3.71 (s, 3H), 3.52-3.48 (d, *J* = 9.9Hz, 1H),

1.88-1.81 (m, 2H), 1.76-1.68 (m, 1H), 1.44-1.37 (m, 1H);
MS(ESI) m/z(relative intensity): 299(M+1), 321(M+Na)
IR(film): 2967, 2854, 1732, 1488, 1204, 1160, 1100, 1009, 817, 760, 506 cm^{-1};

6c Methyl 2-(4-chlorophenyl)-2-tetrahydrofuran-2-yl)acetate; 86%, colorless oil, dr=16.9:1, HPLC (OB-H, 98:2/hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 21.4 min (minor) and 26.8 min (major), 97% ee; $[\alpha]_D^{20}$ -42.1(c = 1.1, $CDCl_3$);
^1H NMR(300 MHz, $CDCl_3$): δ 7.29-7.26 (m, 4H), 4.50-4.42 (m, 1H), 3.94-3.79 (m, 2H), 3.70(s, 3H), 3.51 (d, *J* = 9.6Hz, 1H), 1.92-1.78 (m, 2H), 1.76-1.65 (m, 1H), 1.46-1.34 (m, 1H);
MS(EI) m/z(relative intensity): 254(M, 0.5), 71(100), 43(51), 41(17), 125(13), 184(12), 89(8), 152(7);
IR(neat): 2952, 2873, 1739, 1492, 1206, 1161, 1069, 1016, 824, 732, 514cm^{-1};

6d Ethyl 2-(tetrahydrofuran-2-yl)-2-p-tolylacetate; 74%, colorless oil, dr=14.6:1, HPLC (PC-2, 95:5/Hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 13.0 min (minor) and 14.4 min (major), 95% ee; $[\alpha]_D^{20}$ -33.1(c = 1.0, $CDCl_3$);
^1H NMR(300 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.54-4.46 (m, 1H), 4.25-4.08 (m, 2H), 3.95-3.79 (m, 2H), 3.47 (d, *J* = 9.6Hz, 1H), 2.33 (s, 3H), 1.89-1.79 (m, 2H), 1.74-1.66 (m, 1H), 1.48-1.39 (m, 1H), 1.22 (t, *J* = 7.2Hz, 3H);
^{13}C NMR(100 MHz, $CDCl_3$): δ 173.0, 137.6, 133.3, 129.6, 128.5, 80.9, 68.7, 61.1, 57.5, 29.7, 25.7, 21.3, 14.3;
MS(EI) m/z(relative intensity): 248(M, 0.5), 71(100), 178(65), 43(40), 105(24), 132(12), 175(12), 41(11);
HRMS-EI Calcd for [$C_{15}H_{20}O_3$] 248.1412; Found: 248.1408;
IR(neat): 2978, 2872, 1735, 1514, 1202, 1158, 1069, 1032, 822, 758, 512 cm^{-1};

6e Methyl 2-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)acetate; 22%, colorless oil, dr=2.5:1, HPLC (OB-H, 98:2/Hexane:2-propanol, 0.5 mL/min, 214 nm) retention times of 24.8 min (minor) and 30.3 min (major), 92% ee; $[\alpha]_D^{20}$ -45.8(c = 1.0, $CDCl_3$);
^1H NMR(300 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.7Hz, 2H), 6.85 (d, *J* = 8.7Hz, 2H), 4.52-4.44 (m, 1H), 3.95-3.81 (m, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 3.47 (d, *J* = 9.9Hz, 1H), 1.90-1.65 (m, 3H), 1.48-1.39 (m, 1H);
MS(EI) m/z(relative intensity): 250(M, 2), 71(100), 180(84), 121(27), 43(24), 148(15), 165(14), 135(12);
IR(neat): 2952, 2873, 1737, 1622, 1514, 1253, 1160, 1067, 1034, 831, 753, 532 cm^{-1};

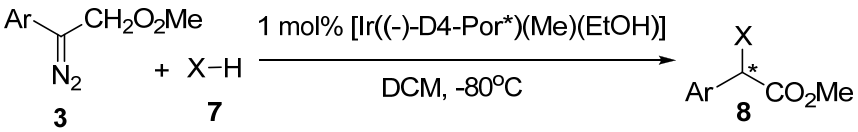
6f Methyl 2-(3-chlorophenyl)-2-(tetrahydrofuran-2-yl)acetate; 86%, colorless oil, dr=13.7:1, HPLC (PA-2, 95:5/Hexane:2-propanol, 0.3 mL/min, 214 nm) retention times of 37.3min (major) and 48.4min (minor), 81% ee; $[\alpha]_D^{20}$ -32.6(c = 1.1, $CDCl_3$);
^1H NMR(300 MHz, $CDCl_3$): δ 7.36 (s, 1H), 7.27-7.23 (m, 3H), 4.52-4.44 (m, 1H),

3.95-3.80 (m, 2H), 3.72 (s, 3H), 3.50 (d, *J* = 9.9Hz, 1H), 1.91-1.69 (m, 3H), 1.58-1.39 (m, 1H);
MS(EI) m/z(relative intensity): 254(M, 0.3), 71(100), 43(27), 41(9), 89(7), 125(7), 152(5), 72(4);
IR(neat): 2952, 2873, 1739, 1596, 1433, 1205, 1162, 1069, 1021, 707, 686 cm^{-1};

6g Methyl 2-(naphthalen-2-yl)-2-(tetrahydrofuran-2-yl)acetate; 76%, colorless oil, dr=9.3:1, HPLC (OD-H, 100:1/Hexane:2-propanol, 0.5 mL/min, 214 nm) retention times of 50.0 min (major) and 70.9 min (minor), 92% ee; $[\alpha]_D^{20}$ -65.2(c = 0.56, $CDCl_3$);
^1H NMR(300 MHz, $CDCl_3$): δ 7.84-7.80 (m, 4H), 7.51-7.46 (m, 3H), 4.69-4.61 (m, 1H), 3.99-3.83 (m, 2H), 3.71-3.69 (m, 4H), 1.92-1.64 (m, 3H), 1.54-1.44 (m, 1H);
MS(EI) m/z(relative intensity): 270(M, 4), 71(100), 200(76), 43(31), 141(28), 168(28), 139(18), 140(15);
IR(neat): 3058, 2953, 2865, 1728, 1598, 1435, 1322, 1198, 1156, 1070, 827, 750cm^{-1};

6h Methyl 2-(tetrahydrofuran-2-yl)-2-(thiophen-3-yl)acetate; 23%, colorless oil, dr >20:1, HPLC (PC-2, 95:5/Hexane:2-propanol, 0.7mL/min, 214 nm) retention times of 14.7 min (minor) and 15.6 min (major), 91% ee; $[\alpha]_D^{20}$ -60.2(c = 0.8, $CDCl_3$);
^1H NMR(300 MHz, $CDCl_3$): δ 7.29-7.27 (m, 1H), 7.22 (s, 1H), 7.10-7.09 (m, 1H), 4.50-4.43 (m, 1H), 3.98-3.78 (m, 2H), 3.72-3.69 (m, 4H), 1.87-1.71 (m, 3H), 1.52-1.45 (m, 1H);
^{13}C NMR(100 MHz, $CDCl_3$): δ 173.0, 136.1, 127.6, 126.1, 123.0, 80.7, 68.8, 53.3, 52.4, 29.9, 25.7;
MS(EI) m/z(relative intensity): 226(M, 1), 71(100), 43(43), 156(28), 41(15), 97(14), 124(9),45(7);
IR(neat): 3103, 2951, 2873, 1737, 1435, 1327, 1198, 1163, 1067, 1022, 842, 779cm^{-1};

Procedure for asymmetric Si-H bond insertion of THF with methyl aryldiazoacetate catalyzed by [Ir((-)-D_4-Por*)(Me)(EtOH)] 2



To a solution of **3** (0.4 mmol) and Et_3SiH or $PhMe_2SiH$ (0.48 mmol) in anhydrous dichloromethane (4 mL), after stirring 10 minutes at -80°C the catalyst **2** (1 mol%) was added. The reaction was stirred for 24 hours at -80°C and then purified by a silica gel column chromatography with dichloromethane /petroleum ether (1:5) as eluent to yield the product **8**.

8a Methyl 2-(dimethyl(phenyl)silyl)-2-phenylacetate; 92%, colorless oil, HPLC (AD-H, 99:1/Hexane:2-propanol, 0.6 mL/min, 230 nm) retention times of 11.0 min (minor) and 13.8 min (major), 72%ee; $[\alpha]_D^{20}$ -16.8(c = 1.0, $CHCl_3$);

^{1}H NMR(300 MHz, $CDCl_3$): δ 7.39-7.30 (m, 5H), 7.22-7.13 (m, 5H), 3.60 (s, 1H), 3.55 (s, 3H), 0.35 (s, 3H), 0.32 (s, 3H);
MS(ESI) (m/z): 302(M+18);
IR(neat): 3025, 2950, 1716, 1600, 1496, 1351, 1250, 1198, 1148, 1072, 814, 700, 501cm^{-1};

8b Methyl 2-(4-bromophenyl)-2-(dimethyl(phenyl)silyl)acetate; 93%, colorless oil, HPLC (PA-2, 90:10/Hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 7.6 min (minor) and 9.0 min (major), 91% ee; $[\alpha]_D^{20}$ -17.6 (c = 1.0, $CHCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.42-7.31 (m, 7H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.58-3.56 (m, 3H), 0.34 (s, 3H), 0.33 (s, 3H);
MS(EI) m/z(relative intensity): 362(M, 2), 135(100), 196(51), 198(50), 89(19), 136(14), 43(13), 105(12);
IR(neat): 3022, 2959, 1710, 1488, 1456, 1331, 1161, 1117, 1072, 1009, 864, 815, 702, 507cm^{-1};

8c Methyl 2-(4-chlorophenyl)-2-(dimethyl(phenyl)silyl)acetate; 75%, colorless oil, HPLC (PA-2, 90:10/Hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 6.2 min (minor) and 7.1 min (major), 78% ee; $[\alpha]_D^{20}$ -19.2(c = 1.0, $CHCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.40-7.33 (m, 5H), 7.19-7.11 (m, 4H), 3.58-3.56 (m, 4H), 0.34 (s,3H), 0.33 (s, 3H);
MS(EI) m/z(relative intensity): 318(M, 0.1), 43(100), 129(13), 171(7), 41(5), 69(4), 111(4), 42(3);
IR(neat): 3050, 2951, 1721, 1491, 1337, 1297, 1267, 1152, 1117, 1092, 1014, 864, 811, 702, 510cm^{-1};
IR(neat): 3049, 2950, 1720, 1429, 1314, 1250, 1220, 1141, 1117, 914, 815, 700cm^{-1};

8d methyl 2-phenyl-2-(triethylsilyl)acetate; 75%, colorless oil, HPLC (PC-1, 80:20/Hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 4.6 min (major) and 6.0 min (minor), 75% ee; $[\alpha]_D^{28}$ 23.4(c = 1.0, $CHCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.5Hz, 2H), 7.27 (t, *J* = 7.8Hz, 3H), 7.16 (t, *J* = 7.2Hz, 3H), 3.68 (s, 3H), 3.53 (s, 1H), 0.90 (t, *J* = 7.8Hz, 9H), 0.59 (q, *J* = 7.8Hz, 6H);
MS(ESI) m/z(relative intensity): 265(M+1), 287(M+Na);
IR(film): 2953, 2877, 1725, 1350, 1278, 1197, 1147, 787, 701cm^{-1};

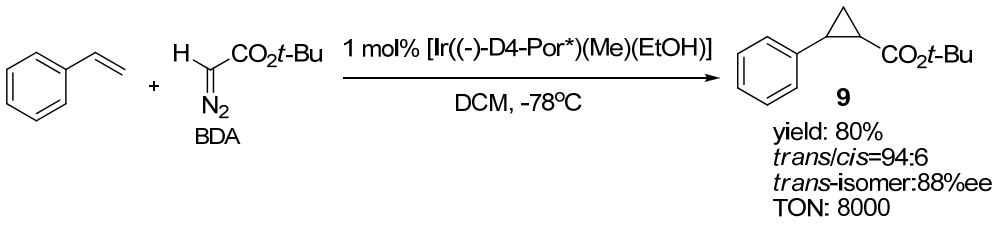
8e methyl 2-(4-bromophenyl)-2-(triethylsilyl)acetate; 93%, colorless oil, HPLC (PA-2, 95:5/Hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 6.2 min (minor) and 7.5 min (major), 91% ee; $[\alpha]_D^{20}$ 31.6(c = 1.0, $CHCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.7Hz, 2H), 7.24 (d, *J* = 8.7Hz, 2H), 3.68 (s, 3H), 3.49 (s, 1H), 0.90 (t, *J* = 7.8Hz, 9H), 0.61-0.53 (m, 6H);
^{13}C NMR(100 MHz, $CDCl_3$): δ 173.5, 136.0, 131.4, 130.4, 119.6, 51.7, 42.5, 7.3, 2.9;
MS(EI) m/z(relative intensity): 198(100), 196(98), 87(66), 89(62), 117(50), 115(34), 59(32), 61(18);

IR(neat): 3020, 2953, 2878, 1724, 1488, 1434, 1337, 1296, 1266, 1197, 1151, 1077, 1010, 825, 710cm^{-1};

8f methyl 2-(4-chlorophenyl)-2-(triethylsilyl)acetate, 94%, colorless oil, HPLC (PA-2, 90:10/Hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 6.0 min (minor) and 6.8 min (major), 82% ee; $[\alpha]_D^{20}$ 27.2(c = 1.1, $CHCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.31-7.23 (m, 4H), 3.68 (s, 3H), 3.51 (s, 1H), 0.90 (t, *J* = 7.8 Hz, 9H), 0.61-0.53 (m, 6H);
MS(EI) m/z(relative intensity): 298(M, 3), 152(100), 87(59), 59(46), 89(40), 154(36), 117(29), 61(24);
IR(neat): 2954, 2878, 1724, 1491, 1434, 1380, 1296, 1267, 1198, 1150, 1092, 1014, 830, 711, 508cm^{-1};

8g methyl 2-(naphthalen-2-yl)-2-(triethylsilyl)acetate; 92%, colorless oil, HPLC (PA-2, 90:10/Hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 6.7 min (minor) and 7.6 min (major), 75%ee; $[\alpha]_D^{20}$ 26.8 (c = 1.0, $CHCl_3$);
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.81-7.75 (m, 4H), 7.52-7.40 (m, 3H), 3.71 (br, 4H), 0.92 (t, *J* = 8.1Hz, 9H), 0.65-0.57 (m, 6H);
^{13}C NMR(100 MHz, $CDCl_3$): δ 173.7, 134.1, 133.4, 131.7, 127.6, 127.5, 127.4, 126.4, 125.8, 125.1, 51.4, 42.8, 7.1, 2.7;
MS(EI) m/z(relative intensity): 314(M, 8), 168(100), 87(20), 140(19), 89(13), 59(12), 139(12), 169(12);
HRMS-EI (m/z) [M], Calcd for [$C_{19}H_{26}O_2Si$] 314.1702; Found: 314.1703;
IR(neat): 3056, 2952, 2877, 1723, 1599, 1507, 1432, 1304, 1157, 1140, 1019, 823, 737, 711cm^{-1};

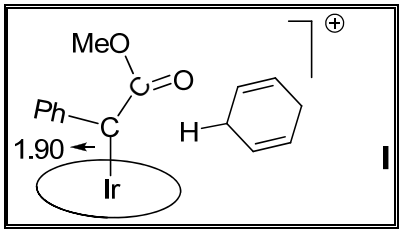
Cyclopropanation of styrene with diazoacetate catalyzed by [Ir((-)-D$_4$-Por*)(Me)(EtOH)] 2



To a solution of styrene **(**4 mmol**)** and catalyst **2** (1 mol%) in anhydrous dichloromethane (4 mL), BDA (0.4 mmol) was added in a period of 1.5 h by syringe pump, the reaction was further stirred for 10 minutes after addition was complete and then purified by a silica gel column chromatography with ethyl acetate/petroleum ether (1:500) as eluent to yield the product **9**.
9 (*trans*)-*tert*-butyl 2-phenylcyclopropanecarboxylate
80%, colorless oil, HPLC (OD-H, 99:1/Hexane:2-propanol, 0.7 mL/min, 214 nm) retention times of 7.3 min (minor) and 7.9 min (major), 88% ee;
^{1}H NMR(300 MHz, $CDCl_3$) δ7.29-7.07 (m, 5H), 2.47-2.40 (m, 1H),1.86-1.80 (m, 1H),

1.60-1.52 (m, 1H), 1.46 (s, 9H), 1.26-1.20 (m, 1H);
(*cis*)-*tert*-butyl 2-phenylcyclopropanecarboxylate
^{1}H NMR(300 MHz, $CDCl_3$): δ 7.26-7.20 (m, 5H), 2.57-2.49 (m, 1H), 1.99-1.94 (m, 1H), 1.65-1.63 (m, 1H), 1.25-1.20 (m, 1H), 1.13 (s, 9H);
IR(film): 3030, 2979, 1728, 1714, 1392, 1367, 1171, 1148, 1079, 697cm^{-1};
MS(EI) m/z (relative intensity): 218(M^+, 2), 162(92), 144(33), 127(10), 117(100), 107(19), 91(15);

Cartesian coordinates, total free energies (Hartree/Particle) of the stationary points found for intermolecular carbene insertion reaction pathway of I and II to the 1,4-cyclohexadiene at the B3LYP/6-31G(d):LANL2DZ level by G09 soft package.[6]



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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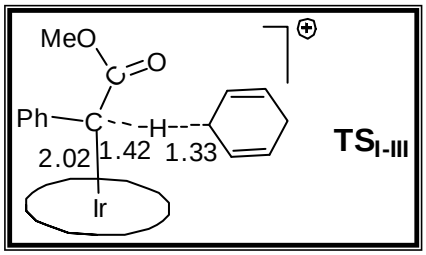
2	6	0	-0.276732	0.845236	2.198202
3	6	0	0.060487	0.724298	3.575112
4	6	0	-0.408658	1.644877	4.500794
5	6	0	-1.256925	2.681078	4.092473
6	6	0	-1.621815	2.799600	2.748254
7	6	0	0.212614	-0.144113	1.260320
8	6	0	0.554629	-1.476936	1.896633
9	8	0	1.675810	-1.777020	2.249114
10	77	0	0.575180	0.031226	-0.596901
11	7	0	0.312284	-1.982867	-0.966053
12	6	0	-0.893329	-2.615036	-1.212019
13	6	0	-0.676388	-4.038227	-1.250263
14	6	0	0.654206	-4.253931	-1.059464
15	6	0	1.278171	-2.968786	-0.876903
16	6	0	-2.119475	-1.981596	-1.449990
17	6	0	-3.329767	-2.835441	-1.677576
18	6	0	-3.457131	-3.599832	-2.848185
19	6	0	-4.590048	-4.387096	-3.058777
20	6	0	-5.606987	-4.422462	-2.102184
21	6	0	-5.488442	-3.663650	-0.935984
22	6	0	-4.358839	-2.871119	-0.723672
23	6	0	2.639813	-2.770244	-0.614752
24	6	0	3.228634	-1.520988	-0.389657
25	7	0	2.590542	-0.290307	-0.401806

26	6	0	3.536358	0.658970	-0.044991
27	6	0	4.796105	0.001480	0.177740
28	6	0	4.613422	-1.325901	-0.058043
29	6	0	3.329075	2.041280	0.038232
30	6	0	2.130101	2.674783	-0.320349
31	7	0	0.947718	2.049964	-0.668618
32	6	0	0.087246	3.040646	-1.124618
33	6	0	0.755732	4.312832	-1.046590
34	6	0	1.996702	4.092264	-0.535389
35	6	0	-1.212930	2.847011	-1.610335
36	6	0	-1.977519	4.047344	-2.078131
37	6	0	-2.381443	5.043931	-1.176069
38	6	0	-3.091287	6.159675	-1.621848
39	6	0	-3.403505	6.296643	-2.976000
40	6	0	-3.004340	5.311976	-3.882186
41	6	0	-2.298292	4.193689	-3.437146
42	6	0	3.512519	-3.985223	-0.512873
43	6	0	3.933204	-4.667485	-1.663443
44	6	0	4.740761	-5.801317	-1.554230
45	6	0	5.132112	-6.265273	-0.296603
46	6	0	4.714683	-5.591455	0.853555
47	6	0	3.909423	-4.456284	0.748265
48	7	0	-1.289332	0.366322	-1.363075
49	6	0	-1.849789	1.597828	-1.684530
50	6	0	-3.214156	1.395937	-2.083023
51	6	0	-3.474153	0.059605	-2.004442
52	6	0	-2.273554	-0.592087	-1.562892
53	6	0	4.475062	2.912653	0.450458
54	6	0	4.429295	3.601980	1.672065
55	6	0	5.489516	4.421027	2.062842
56	6	0	6.604350	4.567827	1.234915
57	6	0	6.655400	3.892115	0.013755
58	6	0	5.598662	3.068552	-0.376692
59	8	0	-0.538902	-2.226445	2.054190
60	6	0	-0.340987	-3.525377	2.666405
61	1	0	7.428288	5.207084	1.538546
62	1	0	5.760116	-7.147606	-0.213242
63	1	0	-6.487899	-5.036414	-2.266242
64	1	0	-3.953860	7.166196	-3.323235
65	1	0	3.579490	-3.929759	1.639746
66	1	0	5.015021	-5.949496	1.834325
67	1	0	5.065523	-6.319316	-2.452125
68	1	0	3.632909	-4.305209	-2.643023
69	1	0	-2.139869	4.941726	-0.121353
70	1	0	-3.401545	6.920193	-0.910931
71	1	0	-3.238202	5.415012	-4.937913
72	1	0	-1.982526	3.433388	-4.146178
73	1	0	-6.275414	-3.686793	-0.187429
74	1	0	-4.678952	-4.968727	-3.971930
75	1	0	-2.671526	-3.567062	-3.598248
76	1	0	3.564042	3.485951	2.319067
77	1	0	5.444704	4.942664	3.014657
78	1	0	7.515902	4.008865	-0.638819
79	1	0	5.637004	2.552099	-1.331909
80	1	0	5.347715	-2.115234	-0.001967
81	1	0	5.708549	0.501955	0.464392
82	1	0	0.331211	5.251301	-1.369377
83	1	0	-3.886924	2.182083	-2.390947

84	1	0	-4.395015	-0.449777	-2.246063
85	1	0	-1.447924	-4.773295	-1.423565
86	1	0	1.178550	-5.197880	-1.048042
87	1	0	-1.332700	-3.972410	2.708620
88	1	0	0.329900	-4.127759	2.051670
89	1	0	0.076571	-3.407454	3.668656
90	1	0	2.780234	4.815223	-0.364695
91	1	0	0.724687	-0.068772	3.901351
92	1	0	-0.121172	1.554208	5.543743
93	1	0	-1.638070	3.388616	4.823089
94	1	0	-2.299290	3.588571	2.436294
95	1	0	-1.430751	1.987584	0.775305
96	6	0	-4.518978	-1.162808	4.187755
97	6	0	-4.099365	-0.701605	2.815534
98	6	0	-4.867845	0.054586	2.024782
99	6	0	-6.244951	0.531052	2.409482
100	6	0	-6.663182	0.067597	3.780785
101	6	0	-5.895934	-0.685873	4.571708
102	1	0	-3.110869	-1.010061	2.476923
103	1	0	-4.501245	0.356987	1.044114
104	1	0	-6.288428	1.632032	2.355752
105	1	0	-7.650019	0.376409	4.121110
106	1	0	-6.261918	-0.986444	5.551918
107	1	0	-4.274569	-2.282341	0.185957
108	1	0	-4.474684	-2.263662	4.243768
109	1	0	-3.782162	-0.823011	4.935478
110	1	0	-6.980066	0.194831	1.659200

Sum of electronic and thermal Free Energies= -2747.969579 (Hartree/Particle)



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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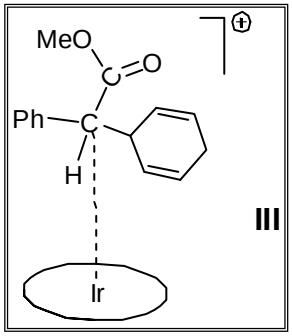
3	6	0	4.814686	3.296837	0.361630
4	6	0	6.002545	4.030126	0.364781
5	6	0	6.743423	4.171621	-0.810719
6	6	0	6.292782	3.576980	-1.991182
7	6	0	3.083683	1.903655	-0.809972
8	6	0	1.876398	2.610038	-0.781993
9	7	0	0.604587	2.063880	-0.754585
10	6	0	-0.286683	3.122339	-0.754689
11	6	0	0.449797	4.360199	-0.782437

12	6	0	1.772168	4.046266	-0.810059
13	77	0	0.129767	0.078381	-0.592089
14	6	0	-1.681532	3.029673	-0.822839
15	6	0	-2.463397	4.309540	-0.802113
16	6	0	-2.663269	4.991898	0.407019
17	6	0	-3.380682	6.189263	0.432037
18	6	0	-3.903915	6.719216	-0.749150
19	6	0	-3.707455	6.047112	-1.957416
20	6	0	-2.991417	4.849087	-1.984728
21	1	0	-4.460193	7.651986	-0.728788
22	1	0	7.666881	4.743633	-0.807465
23	6	0	0.138755	0.139987	1.423906
24	6	0	1.546129	0.412546	1.956813
25	8	0	2.232433	-0.691306	2.294784
26	6	0	3.570031	-0.461061	2.797789
27	6	0	-0.956999	0.811506	2.186521
28	8	0	1.997265	1.534728	2.062800
29	7	0	-1.836825	0.559015	-0.965020
30	6	0	-2.383244	1.827134	-0.978893
31	6	0	-3.797294	1.733633	-1.242241
32	6	0	-4.091669	0.418487	-1.419998
33	6	0	-2.870903	-0.325774	-1.232956
34	6	0	-2.766475	-1.719287	-1.311561
35	6	0	-1.569590	-2.436837	-1.155197
36	7	0	-0.315511	-1.899077	-0.915457
37	6	0	0.576077	-2.960608	-0.855142
38	6	0	-0.151725	-4.191326	-1.008157
39	6	0	-1.461855	-3.869938	-1.209271
40	6	0	1.971795	-2.864589	-0.737473
41	6	0	2.763969	-4.135769	-0.682080
42	6	0	2.869916	-4.971591	-1.804746
43	6	0	3.613505	-6.151087	-1.742381
44	6	0	4.259347	-6.512833	-0.558116
45	6	0	4.163240	-5.686686	0.563407
46	6	0	3.423903	-4.504584	0.500309
47	1	0	4.836625	-7.431640	-0.510637
48	7	0	2.135635	-0.388037	-0.724707
49	6	0	2.683131	-1.657882	-0.735269
50	6	0	4.118134	-1.552502	-0.825273
51	6	0	4.426259	-0.227964	-0.868673
52	6	0	3.186374	0.505687	-0.804901
53	6	0	-4.011877	-2.500084	-1.608111
54	6	0	-5.032249	-2.616419	-0.651654
55	6	0	-6.191592	-3.340929	-0.933111
56	6	0	-6.347951	-3.957433	-2.176210
57	6	0	-5.339579	-3.846367	-3.135887
58	6	0	-4.179040	-3.124137	-2.854176
59	1	0	-7.250960	-4.519369	-2.396452
60	1	0	4.235361	3.180331	1.273367
61	1	0	6.349123	4.490128	1.286077
62	1	0	6.862490	3.687391	-2.909551
63	1	0	4.754199	2.383961	-2.918354
64	1	0	-4.913737	-2.137472	0.316973
65	1	0	-6.971733	-3.424098	-0.181523
66	1	0	-5.457130	-4.317854	-4.107434
67	1	0	-3.399648	-3.033375	-3.605747
68	1	0	3.351639	-3.861244	1.373517
69	1	0	4.663104	-5.961950	1.487897

70	1	0	3.691735	-6.784588	-2.621350
71	1	0	2.376232	-4.689153	-2.730467
72	1	0	-2.259343	4.577913	1.326909
73	1	0	-3.530532	6.707903	1.374925
74	1	0	-4.106792	6.456600	-2.880990
75	1	0	-2.832306	4.332066	-2.927266
76	1	0	2.613364	4.721270	-0.860646
77	1	0	-0.000420	5.341240	-0.810855
78	1	0	-5.047199	-0.018134	-1.669173
79	1	0	-2.287206	-4.544495	-1.382485
80	1	0	0.290049	-5.176318	-0.989496
81	1	0	4.794918	-2.392267	-0.879342
82	1	0	5.403019	0.223851	-0.958539
83	1	0	3.953987	-1.448782	3.050622
84	1	0	4.185515	0.004352	2.027161
85	1	0	3.535556	0.180282	3.681379
86	1	0	-4.466059	2.578090	-1.315948
87	6	0	-0.704157	1.819977	3.144520
88	6	0	-1.749633	2.405950	3.856439
89	6	0	-3.066863	1.987464	3.658775
90	6	0	-3.332240	0.974524	2.732698
91	6	0	-2.294358	0.396780	2.008679
92	1	0	0.305167	2.173306	3.304734
93	1	0	-1.528465	3.193249	4.571511
94	1	0	-3.878025	2.447055	4.216348
95	1	0	-4.352707	0.642757	2.563106
96	1	0	-2.516515	-0.386130	1.298134
97	1	0	-0.064309	-1.181694	1.890083
98	6	0	-0.172107	-2.265040	2.658497
99	6	0	-1.472922	-2.863902	2.345733
100	1	0	0.691216	-2.754254	2.205058
101	6	0	-2.496679	-2.835594	3.223277
102	1	0	-1.589550	-3.349010	1.382918
103	6	0	-2.383754	-2.230661	4.585070
104	1	0	-3.444241	-3.301618	2.961711
105	6	0	-1.004567	-1.761043	4.918796
106	1	0	-3.093285	-1.389630	4.682110
107	1	0	-2.725298	-2.953499	5.344556
108	6	0	0.014394	-1.802637	4.039065
109	1	0	-0.830860	-1.408204	5.932680
110	1	0	1.006894	-1.485031	4.337607

Sum of electronic and thermal Free Energies=-2747.937789



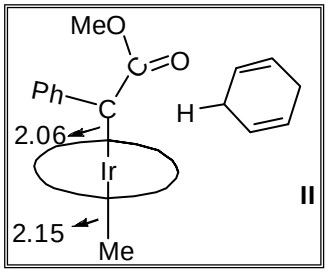
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.482641	2.312106	2.110023
2	6	0	3.394850	1.253697	2.248245
3	6	0	4.751842	1.564157	2.427356
4	6	0	5.177978	2.894388	2.466937
5	6	0	4.259481	3.936887	2.335078
6	6	0	2.906530	3.640373	2.157912
7	6	0	2.848397	-0.171635	2.235265
8	6	0	3.714645	-1.157866	1.461175
9	8	0	3.409273	-1.608972	0.371110
10	77	0	-1.113062	0.077769	-0.880081
11	7	0	-1.429379	-1.965855	-0.833542
12	6	0	-2.512399	-2.617451	-0.313680
13	6	0	-2.288773	-4.045937	-0.321431
14	6	0	-1.069480	-4.252573	-0.875243
15	6	0	-0.531718	-2.953912	-1.218675
16	6	0	-3.686949	-1.998764	0.152821
17	6	0	-4.815399	-2.869976	0.608478
18	6	0	-5.519257	-3.662071	-0.312520
19	6	0	-6.571653	-4.473515	0.113076
20	6	0	-6.929107	-4.508915	1.462798
21	6	0	-6.232024	-3.727292	2.386530
22	6	0	-5.183197	-2.909962	1.962742
23	6	0	0.685544	-2.738868	-1.846407
24	6	0	1.213065	-1.447138	-2.091617
25	7	0	0.667692	-0.215464	-1.661474
26	6	0	1.587367	0.776708	-2.068613
27	6	0	2.621892	0.174759	-2.789755
28	6	0	2.384178	-1.203326	-2.811768
29	6	0	1.496998	2.168942	-1.825657
30	6	0	0.393040	2.769319	-1.242928
31	7	0	-0.776615	2.119471	-0.867753
32	6	0	-1.613676	3.088709	-0.390169
33	6	0	-0.957910	4.377660	-0.424485
34	6	0	0.277960	4.180030	-0.944386
35	6	0	-2.925523	2.875457	0.070808
36	6	0	-3.735096	4.065538	0.481212
37	6	0	-4.079522	4.264718	1.827608
38	6	0	-4.827069	5.379953	2.208489
39	6	0	-5.243836	6.305687	1.249556
40	6	0	-4.907830	6.114313	-0.092534
41	6	0	-4.155274	5.003302	-0.475339
42	6	0	1.485432	-3.915681	-2.297149
43	6	0	0.965390	-4.798317	-3.259410
44	6	0	1.709577	-5.898873	-3.683648
45	6	0	2.976548	-6.136636	-3.145862
46	6	0	3.498452	-5.265773	-2.186535
47	6	0	2.764384	-4.156818	-1.763860
48	7	0	-2.879423	0.367937	-0.114672
49	6	0	-3.508285	1.618756	0.162183
50	6	0	-4.852549	1.380230	0.558811

51	6	0	-5.063164	0.027443	0.584407
52	6	0	-3.858288	-0.622298	0.201553
53	6	0	2.655086	3.019013	-2.235687
54	6	0	3.896894	2.883964	-1.592408
55	6	0	4.975554	3.682578	-1.973305
56	6	0	4.831901	4.615193	-3.003071
57	6	0	3.601251	4.753141	-3.649353
58	6	0	2.516745	3.963768	-3.265926
59	8	0	4.850181	-1.487547	2.096813
60	6	0	5.698803	-2.440665	1.433431
61	1	0	5.674479	5.232944	-3.300157
62	1	0	3.554249	-6.995928	-3.474165
63	1	0	-7.746759	-5.142966	1.793056
64	1	0	-5.827368	7.172200	1.546688
65	1	0	3.164875	-3.483905	-1.010789
66	1	0	4.480939	-5.452224	-1.761806
67	1	0	1.301381	-6.567034	-4.436485
68	1	0	-0.015610	-4.608615	-3.685917
69	1	0	-3.749170	3.550387	2.576994
70	1	0	-5.080087	5.526492	3.254633
71	1	0	-5.233507	6.828170	-0.843649
72	1	0	-3.899365	4.854205	-1.520785
73	1	0	-4.637128	-2.308712	2.684684
74	1	0	-6.501280	-3.755250	3.438482
75	1	0	-7.113607	-5.075357	-0.610740
76	1	0	-5.246672	-3.632631	-1.363953
77	1	0	4.006503	2.173714	-0.778053
78	1	0	5.926247	3.579395	-1.458387
79	1	0	3.484992	5.472691	-4.454693
80	1	0	1.562137	4.066154	-3.774543
81	1	0	2.987080	-1.956283	-3.295993
82	1	0	3.444029	0.698181	-3.254492
83	1	0	-1.398133	5.301246	-0.080209
84	1	0	-5.567449	2.156584	0.787147
85	1	0	-5.978533	-0.486077	0.838063
86	1	0	-2.980792	-4.779634	0.063284
87	1	0	-0.559445	-5.190878	-1.032067
88	1	0	6.569595	-2.552316	2.078980
89	1	0	5.179460	-3.396294	1.324155
90	1	0	5.993447	-2.073056	0.447189
91	1	0	1.056386	4.908998	-1.111799
92	1	0	5.475332	0.764830	2.542305
93	1	0	6.232894	3.113345	2.609366
94	1	0	4.594079	4.969803	2.371045
95	1	0	2.179752	4.441315	2.052123
96	1	0	1.427109	2.090603	1.966535
97	1	0	1.917773	-0.149502	1.658619
98	6	0	2.441524	-0.695499	3.669027
99	6	0	1.768443	-2.043108	3.555832
100	6	0	2.120736	-3.115317	4.269795
101	6	0	3.219802	-3.105688	5.296917
102	6	0	3.882679	-1.761301	5.424745
103	6	0	3.548909	-0.696076	4.692471
104	1	0	0.951778	-2.116408	2.837447
105	1	0	1.585390	-4.053352	4.130069
106	1	0	2.817192	-3.421521	6.273498
107	1	0	4.675316	-1.675126	6.166061
108	1	0	4.068026	0.246968	4.845541

109	1	0	1.688697	0.044112	3.992902
110	1	0	3.970723	-3.875190	5.051557

Sum of electronic and thermal Free Energies= -2747.952615



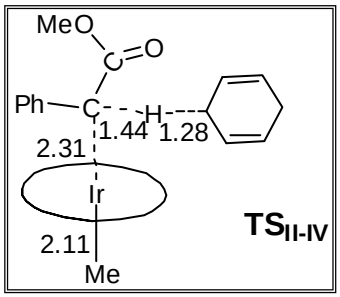
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.461543	-2.193278	2.028736
2	6	0	-0.195462	-0.976643	2.322928
3	6	0	-0.807194	-0.839047	3.596031
4	6	0	-0.787819	-1.883843	4.511747
5	6	0	-0.112912	-3.071500	4.207674
6	6	0	0.524111	-3.214844	2.972270
7	6	0	-0.204715	0.103161	1.343671
8	6	0	-0.216304	1.444216	1.994548
9	8	0	-1.218259	2.040126	2.349659
10	77	0	-0.518489	0.053441	-0.688499
11	7	0	0.184143	1.980041	-0.922611
12	6	0	1.484443	2.339565	-1.181181
13	6	0	1.571913	3.783105	-1.215082
14	6	0	0.318073	4.269476	-1.011343
15	6	0	-0.559785	3.133545	-0.835026
16	6	0	2.558403	1.462043	-1.405531
17	6	0	3.906913	2.062944	-1.669410
18	6	0	4.162923	2.755381	-2.863768
19	6	0	5.418627	3.312838	-3.110135
20	6	0	6.440093	3.185563	-2.166357
21	6	0	6.197839	2.495380	-0.977019
22	6	0	4.942047	1.937453	-0.729473
23	6	0	-1.938910	3.218431	-0.587125
24	6	0	-2.787542	2.122517	-0.368525
25	7	0	-2.420761	0.801103	-0.360066
26	6	0	-3.538281	0.055560	-0.085531
27	6	0	-4.663611	0.947923	0.084257
28	6	0	-4.204928	2.214505	-0.099393
29	6	0	-3.612945	-1.346136	-0.033600
30	6	0	-2.558294	-2.223840	-0.331183
31	7	0	-1.264915	-1.872408	-0.630570
32	6	0	-0.594459	-3.017784	-0.987905
33	6	0	-1.497903	-4.143108	-0.878230
34	6	0	-2.694441	-3.659121	-0.453030
35	6	0	0.746815	-3.097253	-1.400961
36	6	0	1.282895	-4.447027	-1.773318
37	6	0	1.470602	-5.446523	-0.805682
38	6	0	1.966909	-6.701954	-1.160497
39	6	0	2.284756	-6.979942	-2.491388

40	6	0	2.102642	-5.994645	-3.464044
41	6	0	1.606215	-4.739785	-3.107993
42	6	0	-2.538680	4.588449	-0.483040
43	6	0	-2.773742	5.368368	-1.624694
44	6	0	-3.328607	6.644715	-1.510543
45	6	0	-3.654222	7.158272	-0.253482
46	6	0	-3.421716	6.389748	0.889550
47	6	0	-2.867522	5.113464	0.776864
48	7	0	1.318997	-0.683758	-1.244278
49	6	0	1.626018	-2.002176	-1.494879
50	6	0	3.023131	-2.092905	-1.849918
51	6	0	3.529501	-0.829120	-1.830064
52	6	0	2.454314	0.061415	-1.460137
53	6	0	-4.943417	-1.948257	0.314068
54	6	0	-5.365382	-2.009021	1.650576
55	6	0	-6.604235	-2.561212	1.981772
56	6	0	-7.439929	-3.060320	0.980625
57	6	0	-7.030141	-3.004325	-0.353213
58	6	0	-5.791393	-2.451596	-0.683947
59	8	0	1.036258	1.919648	2.139897
60	6	0	1.146942	3.239599	2.707512
61	1	0	-8.404734	-3.489335	1.237950
62	1	0	-4.086392	8.151599	-0.165168
63	1	0	7.418097	3.619210	-2.357954
64	1	0	2.670797	-7.957233	-2.768496
65	1	0	-2.675413	4.512757	1.661762
66	1	0	-3.669444	6.784766	1.871493
67	1	0	-3.509183	7.235750	-2.404689
68	1	0	-2.524874	4.967213	-2.603471
69	1	0	1.224997	-5.233796	0.231302
70	1	0	2.108337	-7.461294	-0.395761
71	1	0	2.342283	-6.203308	-4.503402
72	1	0	1.458777	-3.976896	-3.867289
73	1	0	6.986197	2.390971	-0.236006
74	1	0	5.599375	3.841984	-4.042218
75	1	0	3.371987	2.847808	-3.602986
76	1	0	-4.713708	-1.622824	2.429653
77	1	0	-6.915249	-2.602015	3.022472
78	1	0	-7.676151	-3.387382	-1.138890
79	1	0	-5.475465	-2.403280	-1.722489
80	1	0	-4.766883	3.135920	-0.060214
81	1	0	-5.674279	0.632184	0.297960
82	1	0	-1.241664	-5.167070	-1.106112
83	1	0	3.542571	-3.009054	-2.088843
84	1	0	4.537561	-0.517438	-2.060200
85	1	0	2.479600	4.343740	-1.382366
86	1	0	0.004193	5.302589	-0.981800
87	1	0	2.215836	3.406948	2.838775
88	1	0	0.726953	3.977620	2.020443
89	1	0	0.625916	3.290776	3.666757
90	1	0	-3.603132	-4.211546	-0.264115
91	1	0	-1.325297	0.083509	3.836201
92	1	0	-1.284672	-1.770450	5.471418
93	1	0	-0.081461	-3.879826	4.933440
94	1	0	1.061233	-4.130581	2.740526
95	1	0	0.957728	-2.302513	1.074228
96	6	0	3.814160	-0.464273	3.364522
97	6	0	4.763052	-0.774080	2.235813

98	6	0	6.084220	-0.585781	2.308399
99	6	0	6.783956	-0.046077	3.529722
100	6	0	5.833347	0.271004	4.655636
101	6	0	4.513284	0.083906	4.581167
102	1	0	4.324911	-1.172156	1.321614
103	1	0	6.712137	-0.834297	1.453622
104	1	0	7.544984	-0.767196	3.874068
105	1	0	6.272301	0.671568	5.568562
106	1	0	3.885167	0.333663	5.435485
107	1	0	4.762968	1.399980	0.197622
108	1	0	3.042272	0.242607	3.019542
109	1	0	3.247121	-1.371011	3.634349
110	1	0	7.364259	0.854034	3.263978
111	6	0	-1.068480	0.039228	-2.760768
112	1	0	-2.102960	-0.303761	-2.877600
113	1	0	-0.983659	1.042741	-3.194866
114	1	0	-0.416793	-0.641834	-3.321665

Sum of electronic and thermal Free Energies=-2788.004554



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.328896	2.590977	-1.725618
2	6	0	4.485747	2.492786	-0.609382
3	6	0	4.881280	3.096398	0.594955
4	6	0	6.093985	3.782950	0.677982
5	6	0	6.927145	3.876017	-0.439375
6	6	0	6.541614	3.278410	-1.641143
7	6	0	3.184112	1.751478	-0.676440
8	6	0	2.007359	2.514286	-0.697651
9	7	0	0.724024	2.026079	-0.705339
10	6	0	-0.125675	3.102360	-0.761842
11	6	0	0.654919	4.321188	-0.771958
12	6	0	1.963750	3.959684	-0.739350
13	77	0	0.176060	0.036401	-0.709882
14	6	0	-1.524019	3.049784	-0.875736
15	6	0	-2.259392	4.357168	-0.902845
16	6	0	-2.433655	5.096261	0.277357
17	6	0	-3.108296	6.318433	0.257820
18	6	0	-3.618883	6.820682	-0.940972
19	6	0	-3.450962	6.093464	-2.121206
20	6	0	-2.775872	4.871491	-2.101929

21	1	0	-4.143080	7.772679	-0.955651
22	1	0	7.870772	4.411481	-0.374304
23	6	0	0.074328	0.209821	1.594098
24	6	0	1.449350	0.438140	2.141929
25	8	0	2.108022	-0.697466	2.477303
26	6	0	3.449339	-0.513378	2.961513
27	6	0	-0.992997	0.969213	2.278843
28	8	0	1.973238	1.537325	2.233750
29	7	0	-1.792379	0.587218	-0.958992
30	6	0	-2.277803	1.872898	-1.003720
31	6	0	-3.705478	1.831555	-1.232625
32	6	0	-4.055608	0.524942	-1.362345
33	6	0	-2.851831	-0.259680	-1.188761
34	6	0	-2.790774	-1.661075	-1.250416
35	6	0	-1.621681	-2.424876	-1.096326
36	7	0	-0.356712	-1.937908	-0.846911
37	6	0	0.496889	-3.019260	-0.785284
38	6	0	-0.268145	-4.231383	-0.964144
39	6	0	-1.566124	-3.867513	-1.155947
40	6	0	1.894186	-2.969512	-0.648253
41	6	0	2.627204	-4.276998	-0.598268
42	6	0	3.405122	-4.708890	-1.684322
43	6	0	4.083096	-5.928091	-1.637349
44	6	0	3.993613	-6.738820	-0.503774
45	6	0	3.220895	-6.322414	0.582086
46	6	0	2.544287	-5.102282	0.534004
47	1	0	4.520816	-7.688452	-0.467643
48	7	0	2.161613	-0.507612	-0.636627
49	6	0	2.655820	-1.790233	-0.612252
50	6	0	4.101079	-1.738644	-0.570459
51	6	0	4.458653	-0.427151	-0.606023
52	6	0	3.238745	0.349217	-0.653699
53	6	0	-4.069489	-2.399118	-1.516211
54	6	0	-5.064991	-2.490866	-0.530940
55	6	0	-6.257353	-3.173032	-0.779598
56	6	0	-6.473734	-3.777402	-2.019633
57	6	0	-5.490943	-3.693972	-3.008188
58	6	0	-4.299753	-3.010182	-2.758666
59	1	0	-7.401607	-4.308512	-2.214569
60	1	0	4.230094	3.012168	1.460546
61	1	0	6.389020	4.243669	1.617407
62	1	0	7.182873	3.349587	-2.515947
63	1	0	5.027244	2.129777	-2.662242
64	1	0	-4.895939	-2.023860	0.435828
65	1	0	-7.015811	-3.234429	-0.003288
66	1	0	-5.652627	-4.157119	-3.978098
67	1	0	-3.539318	-2.940502	-3.531538
68	1	0	1.945691	-4.779816	1.381841
69	1	0	3.145928	-6.945669	1.469489
70	1	0	4.677349	-6.246590	-2.489898
71	1	0	3.470159	-4.083566	-2.570390
72	1	0	-2.042536	4.702241	1.211278
73	1	0	-3.236469	6.877567	1.181243
74	1	0	-3.840891	6.478749	-3.059822
75	1	0	-2.639242	4.309990	-3.022141
76	1	0	2.830691	4.603697	-0.751953
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78	1	0	-5.036067	0.118958	-1.563673

79	1	0	-2.413709	-4.513464	-1.332841
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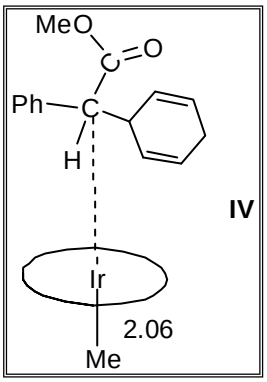
83	1	0	3.798732	-1.512010	3.226246
84	1	0	4.082176	-0.085792	2.182312
85	1	0	3.455733	0.141915	3.837246
86	1	0	-4.345220	2.698943	-1.301880
87	6	0	-0.753968	2.034294	3.182096
88	6	0	-1.808312	2.707440	3.794092
89	6	0	-3.130631	2.321965	3.554767
90	6	0	-3.389798	1.260711	2.683053
91	6	0	-2.340039	0.604528	2.048167
92	1	0	0.263806	2.350395	3.371361
93	1	0	-1.595496	3.531055	4.471024
94	1	0	-3.950530	2.847140	4.038140
95	1	0	-4.413480	0.958454	2.478862
96	1	0	-2.550560	-0.207995	1.367275
97	1	0	-0.219670	-1.130290	2.018387
98	6	0	-0.382370	-2.125232	2.803643
99	6	0	-1.683282	-2.716929	2.439754
100	1	0	0.488609	-2.676976	2.442401
101	6	0	-2.752679	-2.654507	3.253529
102	1	0	-1.759918	-3.206245	1.474046
103	6	0	-2.714383	-2.022347	4.613590
104	1	0	-3.693179	-3.105180	2.941093
105	6	0	-1.336875	-1.585680	5.018601
106	1	0	-3.399804	-1.157394	4.644946
107	1	0	-3.122617	-2.721842	5.362421
108	6	0	-0.275162	-1.658912	4.200270
109	1	0	-1.213408	-1.216200	6.034672
110	1	0	0.704703	-1.347237	4.547848
111	6	0	0.367864	0.140978	-2.808351
112	1	0	-0.353600	0.854123	-3.221819
113	1	0	1.380016	0.463579	-3.076226
114	1	0	0.183775	-0.847361	-3.246788

Sum of electronic and thermal Free Energies= -2787.978681



Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
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2	6	0	-0.969626	-1.764091	3.208360
3	6	0	-1.036544	-2.215169	4.535836
4	6	0	0.104547	-2.694311	5.183032
5	6	0	1.332996	-2.728115	4.521448
6	6	0	1.412510	-2.283771	3.200276
7	6	0	-2.165052	-1.188827	2.451497
8	6	0	-3.445415	-2.002953	2.602052
9	8	0	-3.945574	-2.657844	1.709374
10	77	0	0.724189	0.307791	-1.033983
11	7	0	1.051208	2.269302	-0.558311
12	6	0	2.223752	2.810128	-0.067556
13	6	0	2.032456	4.222113	0.168185
14	6	0	0.757495	4.524083	-0.193006
15	6	0	0.141698	3.304362	-0.661147
16	6	0	3.408130	2.108983	0.199108
17	6	0	4.578176	2.896687	0.709758
18	6	0	5.291235	3.751394	-0.144654
19	6	0	6.381262	4.484472	0.327664
20	6	0	6.774412	4.375595	1.663130
21	6	0	6.070910	3.529838	2.523248
22	6	0	4.981488	2.796257	2.050149
23	6	0	-1.178564	3.200332	-1.121086
24	6	0	-1.793969	2.006817	-1.524528
25	7	0	-1.212717	0.754135	-1.522590
26	6	0	-2.165079	-0.132963	-1.986134
27	6	0	-3.381227	0.586930	-2.281994
28	6	0	-3.151632	1.898804	-2.006441
29	6	0	-2.000228	-1.515869	-2.142028
30	6	0	-0.827175	-2.221377	-1.847272
31	7	0	0.350324	-1.678886	-1.371297
32	6	0	1.248606	-2.719352	-1.243318
33	6	0	0.610663	-3.950971	-1.649473
34	6	0	-0.661678	-3.645895	-2.015699
35	6	0	2.574911	-2.610544	-0.802236
36	6	0	3.384239	-3.871017	-0.719595
37	6	0	3.129291	-4.818533	0.284065
38	6	0	3.882523	-5.991353	0.362576
39	6	0	4.901138	-6.235017	-0.561128
40	6	0	5.162935	-5.299052	-1.563852
41	6	0	4.410352	-4.125927	-1.641991
42	6	0	-2.000399	4.454061	-1.164024
43	6	0	-1.747890	5.445615	-2.124124
44	6	0	-2.513828	6.612156	-2.161571
45	6	0	-3.542825	6.805393	-1.237598
46	6	0	-3.801573	5.825420	-0.276890
47	6	0	-3.037208	4.657848	-0.239878
48	7	0	2.618965	-0.159349	-0.416375
49	6	0	3.197177	-1.413752	-0.416445
50	6	0	4.554643	-1.309703	0.066900
51	6	0	4.789938	0.002259	0.334103
52	6	0	3.575891	0.726353	0.038172
53	6	0	-3.173279	-2.301997	-2.653991
54	6	0	-4.035355	-2.956552	-1.760967
55	6	0	-5.123404	-3.686771	-2.245073
56	6	0	-5.363110	-3.772483	-3.618136

57	6	0	-4.509368	-3.121868	-4.511526
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65	1	0	-3.237759	3.896771	0.509783
66	1	0	-4.598213	5.970351	0.448271
67	1	0	-2.307653	7.368058	-2.914856
68	1	0	-0.949527	5.294446	-2.845563
69	1	0	2.339695	-4.627531	1.005910
70	1	0	3.673872	-6.713205	1.147862
71	1	0	5.951498	-5.482513	-2.288979
72	1	0	4.612342	-3.400357	-2.425201
73	1	0	4.432477	2.141957	2.721814
74	1	0	6.367020	3.442585	3.565365
75	1	0	6.924563	5.138433	-0.349427
76	1	0	4.988357	3.834650	-1.184834
77	1	0	-3.859118	-2.888015	-0.690598
78	1	0	-5.784854	-4.187811	-1.543096
79	1	0	-4.688040	-3.183656	-5.581947
80	1	0	-2.755277	-1.885296	-4.726354
81	1	0	-3.835004	2.727894	-2.115947
82	1	0	-4.288165	0.134583	-2.655711
83	1	0	1.085961	-4.920685	-1.651583
84	1	0	5.234577	-2.140890	0.182044
85	1	0	5.700444	0.448841	0.705389
86	1	0	2.780580	4.886573	0.574770
87	1	0	0.263740	5.483062	-0.138774
88	1	0	-5.515848	-2.458379	5.047435
89	1	0	-5.974098	-2.308840	3.317378
90	1	0	-5.044338	-3.724574	3.864108
91	1	0	-1.430349	-4.316062	-2.371559
92	1	0	-1.984233	-2.194829	5.061989
93	1	0	0.029686	-3.041875	6.210421
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95	1	0	2.359994	-2.303654	2.668351
96	1	0	0.340907	-1.486257	1.517255
97	1	0	-1.937758	-1.271236	1.384075
98	6	0	-2.386531	0.354576	2.715504
99	6	0	-3.516304	0.872543	1.856582
100	6	0	-4.551650	1.572655	2.330265
101	6	0	-4.709022	1.953673	3.777890
102	6	0	-3.570107	1.464877	4.631273
103	6	0	-2.549184	0.743204	4.162996
104	1	0	-3.466449	0.637608	0.794735
105	1	0	-5.332859	1.900837	1.645682
106	1	0	-4.804242	3.048908	3.868143
107	1	0	-3.601939	1.727209	5.687907
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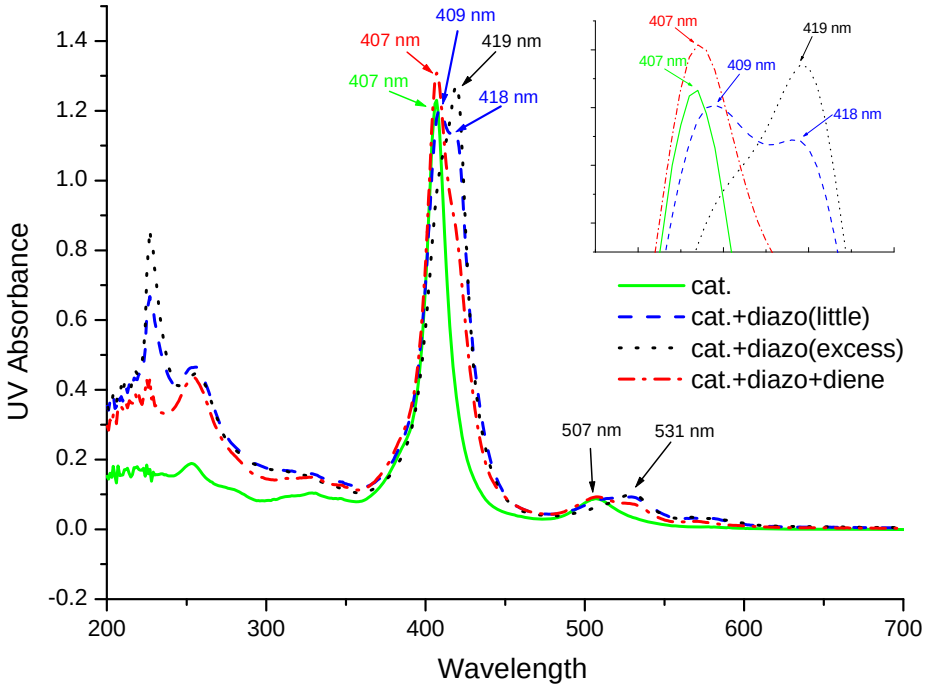
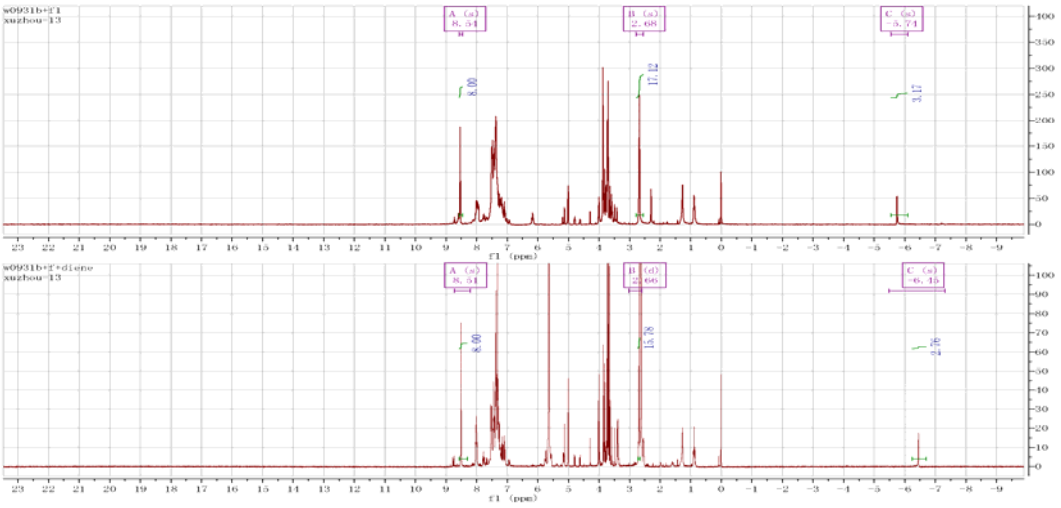
110	1	0	-5.665370	1.564585	4.166999
111	6	0	1.343478	0.534491	-2.990565
112	1	0	2.119857	-0.206504	-3.200868
113	1	0	0.485969	0.377288	-3.650862
114	1	0	1.740662	1.545284	-3.120559

Sum of electronic and thermal Free Energies=-2788.074564

UV and ^{1}H NMR experiment



Procedure: The solution of the catalyst [Ir(TTP)Me] was diluted to ~10^{-7}M, which gave the green UV spectrum; when **3a** (~1 eq.) was added the Soret band partly shifted as indicated by the blue UV spectrum; When excess methyl 2-diazo-2-phenylacetate (10 eq.) was added, the black curve was observed and the Soret band fully shifted. Finally, when excess cyclohexa-1,4-diene (15 eq.) was added, the red UV spectrum was obtained and the Soret band shifted back to the initial position.



Procedure: The solution of [Ir(TTP)Me](4 mg) in $CDCl_3$ and the solution of **3a** (10

eq.) in $CDCl_3$ was separately placed in the NMR tube at -60°C for 5 minutes, then was mixed at this temperature followed by putting into NMR instrument promptly. The coordinated methyl peak shifted from -6.30 ppm to -5.71 ppm. When excess cyclohexa-1,4-diene was added, the peak shifted back to -6.45 ppm.

1 H. M. L. Davies, and T. Hansen, *J. Am. Chem. Soc.*, 1997, **119**, 9075.
2 (a) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.* 1967, **32**, 476; (b) J. S. Lindsey, K. A. Maccrum, J. S. Tyhonas and Y. Y. Chuang, *J. Org. Chem.* 1994, **53**, 579; (c) J. P. Collman, P. D. Hampton and J. I. Brauman, *J. Am. Chem. Soc.* 1990, **112**, 2986; (d) R. L. Halterman and S. T. Jan, *J. Org. Chem.* 2002, **56**, 5253.
3 (a) H. Ogoshi, J.-I. Setsune and Z.-I. Yoshida, *J. Organomet. Chem.* 1978, **159**, 317; (b) S. K. Yeung and K. S. Chan, *Organometallics* 2005, **24**, 6426.
4. H. Suematsu and T. Katsuki, *J. Am. Chem. Soc.*, 2009, **131**, 14218

Figure S1 X-ray crystal structure of [Ir((-)-D_4-Por*)(Me)(EtOH)] **2** (CCDC 790901 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif)

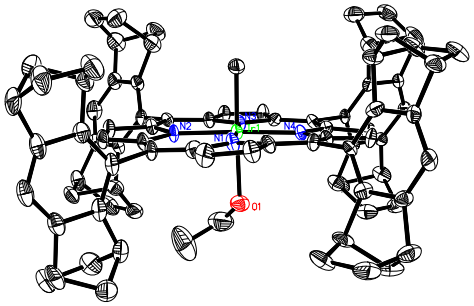


Table 1. Crystal data and structure refinement for cd201129.

Identification code	cd201129	
Empirical formula	C90 H93 Cl4 Ir N4 O2	
Formula weight	1596.71	
Temperature	298 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1	
Unit cell dimensions	a = 9.8320(5) Å	• = 90° .
	b = 28.1647(16) Å	• = 102.4440(10)° .
	c = 14.3172(8) Å	• = 90° .
Volume	3871.5(4) Å^3	

Z	2
Density (calculated)	1.370 Mg/m^3
Absorption coefficient	1.914 mm^{-1}
F(000)	1644
Crystal size	0.2 x 0.1 x 0.05 mm^3
Theta range for data collection	1.63 to 26.00° .
Index ranges	-9<=h<=12, -34<=k<=34, -17<=l<=15
Reflections collected	21209
Independent reflections	14421 [R(int) = 0.0347]
Completeness to theta = 26.00°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.80
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14421 / 20 / 865
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0508, wR2 = 0.1186
R indices (all data)	R1 = 0.0589, wR2 = 0.1219
Absolute structure parameter	-0.010(8)
Largest diff. peak and hole	1.804 and -1.248 $e.Å^{-3}$