Dirhodium(II) Tetrakis[methyl 2-oxaazetidine-4-carboxylate]: A Chiral Dirhodium(II) Carboxamidate of Exceptional Reactivity and Selectivity

Michael P. Doyle,* Simon B. Davies, and Wenhao Hu

Department of Chemistry, University of Arizona, Tucson, Arizona 85721 U.S.A.
mdoyle@u.arizona.edu

Supplementary Information

General. ^{1}H NMR (250 MHz, 300 MHz or 500MHz) and ^{13}C NMR (62.5 MHz, 75 MHz or 125 MHz) spectra were obtained as solutions in $CDCl_3$, and chemical shifts are reported in parts per million (ppm, δ) downfield from the internal standard, Me_4Si (TMS). Mass spectra were obtained using electron ionization on a quadrapole instrument. Infrared spectra were recorded as indicated, either as a thin film on sodium chloride plates or as solutions; absorptions are reported in wavenumbers (cm^{-1}). Melting points are uncorrected. Elemental analyses were performed at Texas Analytical Laboratories Inc. Retention times are recorded in minutes. Anhydrous THF was distilled over sodium / benzophenone; dichloromethane was doubly distilled over calcium hydride for use in catalytic diazo decompositions. Methanesulfonyl azide was prepared by reaction of methanesulfonyl chloride with sodium azide and was not distilled. [1] The preparation of enantiopure catalysts Rh_2(4*S*-MEOX)$_4$, [2] Rh_2(4*S*-MPPIM)$_4$, [3] Rh_2(5*S*-MEPY)$_4$ [4] and Rh_2(4*S*-TBPRO)$_4$ [5] were carried out as previously described. Unless otherwise stated, all chemicals were purchased from Aldrich Chemical Company.

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Synthesis of Di-(2-methyl-l-propyl) L-Aspartate. *p*-Toluenesulphonic acid (100 mmol) was added to a solution of L-aspartic acid (100 mmol) in benzene (30 mL) and 2-methyl-l-propanol (60 mL). The reaction mixture was heated at reflux under Dean-Stark conditions until no further water was extruded from the reaction mixture. Solvent was removed *in vacuo* to afford the tosylate salt as a white solid, which was subsequently dissolved in a solution made up of H_2O (100 mL), 100 mL of a 50% saturated solution of K_2CO_3, and 300 mL of ethyl acetate (EtOAc). The mixture was stirred at 0°C for 30 minutes to generate the free amine. The organic layer was separated and the aqueous layer was extracted with EtOAc (50 mL). The combined organic solution was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford the desired diester as a clear oil (14.94 g, 70 mmol, 61 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.93-3.80 (comp, 5 H), 2.84 (dd, J = 16.5, 4.8 Hz, 1 H), 2.71 (dd, J = 16.5, 7.1 Hz, 1 H), 1.97-1.87 (comp, 2 H), 1.76 (br s, 2 H), 0.93 (d, J = 6.7 Hz, 12 H); GC (SPB-5) t_R 15.33 min (flow 80 psi, 100°C for 2 minutes then 10°C / min to 275°C.

Synthesis of 2-Methyl-l-propyl (*S*)-(-)-2-Oxaazetidine-4-carboxylate. Triethylamine (1.13 mL, 8.1 mmol) was added over 30 minutes to a solution of di-(2-methyl-l-propyl)-L-aspartate (2.16 g, 8.1 mmol) and freshly distilled chlorotrimethylsilane (TMSCl) (8.1 mmol) in dry tetrahydrofuran (THF) (65 mL) at 0°C. [6] The resulting solution was stirred at 0°C for 30 minutes, then at room temperature for a further 2 hours. After re-cooling to 0°C *tert*-butyl magnesium chloride [7] (1.0 M solution in THF, 16.2 mL, 16.2 mmol) was added *via* syringe pump over 1 hour. The reaction mixture was allowed to warm to room temperature over 16 hours, after which time the solvent was removed *in vacuo*. The brown residue was dissolved in EtOAc (100 mL) and washed with 1 % aqueous HCl (65 mL). The aqueous layer was re-extracted with EtOAc (2 x 20 mL), and the combined organic fractions were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification on silica gel (40 % ethyl acetate in hexanes) furnished the title compound (1.0 g, 5.8 mmol, 72%) as a pale yellow oil: $[\alpha]_D^{29}$ = - 44.61 (*c* 1.18,

[6] The general procedure for the synthesis of **2** involves the use of about 30 ml THF per gram of di-ester. Et_3N is added dropwise over 30 minutes. The work up procedure involves the use of 30 ml of 1% aqueous HCl per gram of starting di-ester. This methodology was applied to all oxoazetidine syntheses described within.

[7] It is imperative that the molarity of the *tert*-butylmagnesium chloride be determined prior to its use in this cyclization reaction. General procedure for determination of molarity of *tert*-butylmagnesium chloride: 1,10-phenanthroline (3 mg) was added to stirred solution of *tert*-butylmagnesium chloride (3 ml) in anhydrous THF (3 mL) at room temperature, to generate a

CH_3CN); ^1H NMR (300 MHz, $CDCl_3$) δ 6.40 (br s, 1 H), 4.20 (dd, *J* = 5.7, 2.4 Hz, 1 H), 3.97 (d, *J* = 6.6 Hz, 2 H), 3.34 (ddd, *J* = 14.9, 5.9, 1.2 Hz, 1 H), 3.07 (ddd, *J* = 14.9, 2.7, 2.2 Hz, 1 H), 1.99 (m, 1 H), 0.94 (d, *J* = 6.6 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 166.5, 71.7, 47.3, 43.5, 27.6, 18.9; GC (SPB-5) t_R 13.19 min, (flow 80 psi, 100°C for 2 minutes then 10°C / min to 275°C; Anal. Calcd for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18 %. Found: C, 56.17; H, 7.61; N, 8.12 %.

Generation of Diazomethane. *The preparation of diazomethane was carried out using a "Diazald Kit".* [8] *The kit is designed with smooth glass joints, to minimise the possibility of explosion resulting from the ignition of diazomethane from rough glass surfaces / interfaces. Diazomethane was distilled as an ethereal solution, and used immediately.* A solution of *N*-methyl-*N*-nitroso-*p*-toluene sulfonamide (Diazald) (4.30 g, 20 mmol) in diethyl ether (Et_2O) (50 mL) was added in a dropwise manner to a stirred solution of potassium hydroxide (5.00 g), 95% ethanol (25 mL) and distilled water (8 mL), at 65°C. The rate of addition was equal to the rate of distillation of the ethereal solution of diazomethane, hence avoiding a build up of diazomethane in the reaction vessel. On completion of addition, a further 20 mL of Et_2O was added to the reaction mixture to flush through any residual diazomethane. The receiver flask was connected to a 'scrubber' system, consisting of three traps. The first trap was empty at 0°C, the second contained Et_2O at 0°C and the third contained glacial acetic acid at room temperature. On completion of the procedure the collection flask was removed and the diazomethane generated was stored over potassium hydroxide (3 g) for 1 hour before use. The reaction apparatus was then flushed with glacial acetic acid, destroying any residual diazomethane.

Synthesis of Methyl (*S*)-(-)-2-Oxaazetidine-4-carboxylate. Ethereal diazomethane (70 ml, 20 mmol) was added over 10 minutes *via* dropping funnel to a cooled (0°C) suspension of 4-(*S*)-methyl 2-oxaazteidine carboxylic acid (1.0 g, 8.7 mmol) in Et_2O (30 mL). After complete addition the yellow solution was allowed to warm to room temperature overnight. After removal of solvents and excess diazomethane *in vacuo* (distilled onto acetic acid in solvent trap) the crude yellow oil was purified by

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deep purple solution. This mixture was titrated with freshly distilled isopropyl alcohol, and the molarity of *tert*-butylmagnesium chloride could hence be determined (pale yellow solution at end-point).

[8] Diazald apparatus was purchased from Aldrich Chemical Co.

flash column chromatography on silica gel eluting with ethyl acetate, to afford the title compound as a pale oil (1.03 g, 8.0 mmol, 93 %): $[\alpha]_D^{23}$ = -51.9 (*c*, 0.7 CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.67 (br s, 1 H), 4.20 (dd, *J* = 6.0, 2.4 Hz, 1 H), 3.79 (s, 3 H), 3.33 (ddd, *J* = 15.0, 6.0, 1.5 Hz, 1 H), 3.07 (ddd, *J* = 15.0, 2.4, 1.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 166.6, 52.5, 47.1, 43.4; HRMS (FAB^+): Calcd. For $C_5H_7O_3N$: 130.0504 (M^{+1}). Found: 130.0508 (M^{+1}).

General Procedure for the Synthesis of Dirhodium(II) Carboxamidates. Dirhodium(II) acetate (0.75 mmol), oxaazetidine (6.0 mmol) and chlorobenzene (15 mL) were mixed in a round bottom flask fitted with a Soxhlet extraction apparatus into which was placed a celluose thimble containing 2:1 Na_2CO_3 - sand. The resulting mixture was heated at reflux for 5 hours, at which time HPLC analysis (μ-Bondapak-CN reverse phase column, 1 % MeCN in MeOH, flow 1.0 mL / min) showed the reaction to be complete. After cooling to room temperature the solvent was removed under *vacuo*, and the resulting royal blue solid was chromatographed on BAKERBOND Cyano 40 μm reverse phase silica,[9] initially eluting with MeOH to remove unreacted oxaazetidine ligand (brown band), then 1 % MeCN in MeOH to remove the desired catalyst, which elutes as a red band. The purity of the isolated catalyst was rechecked by HPLC using the conditions described to monitor the reaction.

Synthesis of Dirhodium(II) Tetrakis[methyl 2-oxaazetidine-4(*S*)-carboxylate], Rh_2(4*S*-MEAZ)$_4$ (4). Treatment of dirhodium(II) acetate (0.43 g, 0.96 mmol) with methyl (*S*)-(-)-2-oxaazetidine-4-carboxylate (1.0 g, 7.75 mmol) in chlorobenzene (25 mL) as described in the general procedure and subsequent purification, afforded **4** (370 mg, 0.43 mmol, 53 %) as a purple solid: $[\alpha]_D^{24}$ = -214 (*c* 0.7, CH_3CN); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.01 (comp, 2 H), 3.92 (comp, 2 H), 3.80 (s, 6 H), 3.76 (s, 6 H), 3.40 – 3.23 (comp, 8 H), 2.25 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.8, 188.2, 173.4, 173.3, 115.3, 52.9, 52.1, 52.0, 51.9, 43.5, 42.6, 2.4.

[9] The column must be packed in small steps as a slurry to ensure uniformity of the silica. The chromatography procedure can be rapidly accelerated by pulling solvent through the column using a vacuum. Standard flash methodology using a positive pressure has negligible effect on the flow rate.

Synthesis of Dirhodium(II) Tetrakis[2-methylpropyl 2-Oxaazetidine-4(*S*)-carboxylate], Rh_2(4*S*-IBAZ)$_4$. Treatment of dirhodium(II) acetate (0.33 g, 0.75 mmol) with 2-methyl-l-propyl (*S*)-(-)-2-oxaazetidine-4-carboxylate (1.0 g, 6.0 mmol) in chlorobenzene (15 mL), as described in the general procedure, and subsequent purification afforded Rh_2(4*S*-IBAZ)$_4$ (323 mg, 0.36 mmol, 50 %) as a purple solid: $[\alpha]_D^{25}$ = -211.4 (*c* 0.69, CH_3CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00-3.88 (comp, 12 H), 3.37-3.21 (comp, 8 H), 2.01-1.92 (comp, 4 H), 0.96 (d, *J* = 5.2 Hz, 12 H), 0.93 (d, *J* = 5.2 Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) 188.4, 188.0, 173.2, 173.1, 115.1, 71.1, 52.8, 51.9, 43.4, 42.8, 27.8, 27.7, 19.2, 19.1; Anal. Calcd for $C_{36}H_{54}N_6O_{12}Rh_2$: C, 44.64; H, 5.62; N, 8.68%. Found: C, 44.57; H, 5.53; N, 8.61%.

Synthesis of Dirhodium(II) Tetrakis[benzyl 2-oxaazetidine-4(*S*)-carboxylate], Rh_2(4*S*-BNAZ)$_4$. Treatment of dirhodium(II) acetate (0.40 g, 0.91 mmol) with benzyl (*S*)-(-)-2-oxaazetidine-4-carboxylate (1.5 g, 7.30 mmol) in chlorobenzene (25 mL) as described in the general procedure and subsequent purification, afforded Rh_2(4*S*-BNAZ)$_4$ (490 mg, 0.47 mmol, 52 %) as a purple solid: $[\alpha]_D^{23}$ = -213 (*c* 0.8, CH_3CN); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.26 (comp, 20 H), 5.25 (d, *J* = 12.4 Hz, 2 H), 5.17 (d, *J* = 12.4 Hz, 2 H), 5.10 (d, *J* = 6.5 Hz, 2 H), 5.07 (d, *J* = 6.5 Hz, 2 H), 4.00 (comp, 2 H), 3.86 (comp, 2 H), 3.33 – 3.09 (comp, 8 H), 1.71 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.9, 188.3, 172.9, 172.8, 136.2, 135.6, 128.7 – 127.9, 115.2, 66.6, 52.9, 52.1, 43.4, 42.7, 1.8.

Synthesis of Dimethyl Diazomalonate (5). Mesyl azide (4.0 g, 33 mmol) was added to a solution of dimethyl malonate (3.45 g, 26.1 mmol) and sodium carbonate (8.5 g, 61.5 mmol) in CH_3CN (20 mL). The resulting mixture was stirred for 48 h at room temperature. The solid precipitate was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with 10 % ethyl acetate in hexanes to furnish the desired product (3.0 g, 18.7 mmol, 72 %) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 52.5.

Cyclopropanation of Allyl Styryl Diazoacetate. Procedure. A solution of allyl styryl diazoacetate **8**[10] (91.2 mg, 0.4 mmol) in dichloromethane (CH_2Cl_2) (2 mL) was added *via* syringe pump (1.0 mL/hr) over 2 hours to a refluxing solution of Rh_2(4*S*-MEAZ)$_4$ (7.0 mg, 2.0 mol %) in CH_2Cl_2 (4 mL). After complete addition the reaction mixture was stirred at reflux for a further 30 minutes to ensure complete reaction. The mixture was then cooled to room temperature, then passed through a short silica plug, which was subsequently washed with CH_2Cl_2 (40 mL). Removal of solvent at reduced pressure furnished the crude cyclopropane **9**, which was purified by silica gel column chromatography (Hexane : ethyl acetate 10 : 1) to furnish a colorless oil (48 mg, 0.24 mmol, 59 %).[11] Achiral G.C on a 30-m SPB-5 column. 100°C for 2 min., then 10°C/min to 275°C. t_R = 18.9 min. Cyclopropane **9** (48 mg, 0.24 mmol) was dissolved in MeOH (10 mL), and 10 % Pd/C catalyst was added. The resulting mixture was hydrogenated under H_2 (2 atm.) for 30 minutes, after which time the catalyst was removed by filtration through a short celite plug. The celite was washed with MeOH (10 mL), and the solvent was removed under reduced pressure, to furnish **9** as a colorless oil (45 mg, 0.22 mmol, 93 %), 58 % ee (determined by GC on a 30-m Chiraldex B-DM column, 130°C for 5 min, then 1°C/min to 170°C, $t_{R\ minor}$ = 55.4 min, $t_{R\ major}$ = 56.6 min), achiral GC on a 30-m SPB-5 column. 100°C for 2 min., then 10°C/min to 275°C. t_R = 16.9 min. Data for **9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.18 (comp, 5H), 4.10 – 4.05 (comp, 2 H), 3.82 (t, *J* = 7.8 Hz, 2 H), 2.41 (dt, *J* = 14.2, 7.8 Hz, 1 H), 1.71 (comp, 1 H), 1.68 (dt, *J* = 14.2, 7.8 Hz, 1 H), 1.03 (dd, *J* = 7.4, 4.6 Hz, 1 H) 0.86 (t, *J* = 4.6 Hz, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (C=O not observed), 141.2, 128.4, 126.1, 68.3, 33.1, 30.8, 27.4, 22.6, 17.5; IR ($CDCl_3$): 1764 (C=O); HRMS (FAB$^+$): Calcd for $C_{13}H_{15}O_2$: 203.1072. Found: 203.1069.

Cyclopropanation of Styrene with Dimethyl Diazomalonate. General procedure. A solution of dimethyl diazomalonate **5** (63 mg, 0.39 mmol) in dichloromethane (CH_2Cl_2) (2 mL) was added *via* syringe pump (1.0 mL/hr) over 2 hours to a refluxing solution of Rh_2(4*S*-MEAZ)$_4$ (4.3 mg, 1.0 mol %) and styrene (0.40 ml, 3.9 mmol) in CH_2Cl_2 (4 mL). After complete addition the reaction mixture was stirred at reflux for a further 30 minutes to ensure complete reaction. The mixture was then cooled to room temperature, then passed through a short silica plug, which was subsequently washed with CH_2Cl_2

[10] Davies, H. M. L.; Doan, B. D. *J. Org. Chem.*, **1999**; *64*; 8501-8508.
[11] Data for **9** consistent with published data, see ref. 11

(40 mL). The solvent was removed at reduced pressure, to furnish the desired cyclopropane **6,** Z = Ph (89 mg, 0.38 mmol, 97%) as a colorless oil, 44% ee (determined by GC on a 30-m Chiraldex B-DM column, 100°C for 5min, then 1°C/min to 160°C. $t_{R\ minor}$ = 63.4 min, $t_{R\ major}$ = 64.7 min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.15 (comp, 5 H), 3.78 (s, 3 H), 3.35 (s, 3 H), 3.23 (dd, *J* = 9.3, 7.8 Hz, 1 H), 2.20 (dd, *J* = 7.8, 5.4 Hz, 1 H), 1.74 (dd, *J* = 9.3, 5.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 166.9, 134.5, 128.3, 128.0, 127.2, 52.6, 52.0, 37.1, 32.4, 18.9.

Cyclopropanation of Vinyl Acetate with Dimethyl Diazomalonate. General procedure. A solution of dimethyl diazomalonate **5** (63 mg, 0.39 mmol) in dichloromethane (CH_2Cl_2) (2 mL) was added *via* syringe pump (1.0 mL/hr) over 2 hours to a refluxing solution of Rh_2(4*S*-MEAZ)$_4$ (2.8 mg, 1.0 mol %) and vinyl acetate (0.34 ml, 3.9 mmol) in CH_2Cl_2 (4 mL). After complete addition the reaction mixture was stirred at reflux for a further 30 minutes to ensure complete reaction. The mixture was then cooled to room temperature, then passed through a short silica plug, which was subsequently washed with CH_2Cl_2 (40 mL). The crude product was purifed by flash column chromatography on silica gel eluting with 10 % ethyl acetate in hexanes to furnish the desired cyclopropane **6,** Z = OAc (56 mg, 0.26 mmol, 65%) as a colorless oil, 33 % ee (determined by GC on a 30-m Chiraldex G-PN column, 100°C for 5 min, then 1°C/min to 160°C, $t_{R\ minor}$ = 33.8 min, $t_{R\ major}$ = 34.2 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (dd, *J* = 7.0, 5.2 Hz, 1 H), 3.78 (s, 3 H), 3.75 (s, 3 H), 2.04 (s, 3 H), 1.95 (dd, *J* = 7.0, 5.2 Hz, 1 H), 1.72 (dd, *J* = 7.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 168.4, 165.8, 56.8, 52.8, 33.9, 20.4, 19.3; HRMS (FAB^+) Calcd for $C_9H_{16}O_6$: 217.0712. Found : 217.0714.

Cyclopropanation of *p*-Trifluoromethylstyrene with Dimethyl Diazomalonate. General Procedure. A solution of dimethyl diazomalonate **5** (32 mg, 0.20 mmol) in dichloromethane (CH_2Cl_2) (2 mL) was added *via* syringe pump (0.5 mL/hr) over 4 hours to a refluxing solution of Rh_2(4*S*-MEAZ)$_4$ (1.4 mg, 1.0 mol %) and *p*-trifluoromethylstyrene (0.34 ml, 2.0 mmol) in CH_2Cl_2 (4 mL). After complete addition the reaction mixture was stirred at reflux for a further 30 minutes to ensure complete reaction. The mixture was then cooled to room temperature, then passed through a short silica plug, which was subsequently washed with CH_2Cl_2 (40 mL). The crude product was purifed by flash column

chromatography on silica gel eluting with 40% ethyl acetate in hexanes to furnish the desired cyclopropane **6,** Z = *p*-$CF_3C_6H_4$ (44 mg, 0.14 mmol, 73 %) as a colorless oil, 50 % ee (determined by GC on a 30-m Chiraldex B-DM column, 100°C for 5 min, then 0.5°C/min to 170°C, $t_{R\ minor}$ = 88.9 min, $t_{R\ major}$ = 91.2 min): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 2 H), 3.80 (s, 3 H), 3.38 (s, 3 H), 3.25 (dd, J =9.0, 7.8 Hz, 1 H), 2.20 (dd, J = 7.8, 5.1 Hz, 1 H), 1.78 (dd, J = 9.0, 5.1 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 166.7, 138.8, 128.8, 125.1, 125.0, 52.9, 52.4, 37.3, 31.8, 29.7, 19.1.

Synthesis of Allyl Phenyldiazoacetate (10). A solution of allyl alcohol (20 mL) and Et_3N (3.03 g, 30 mmol) was cooled (0°C) before the dropwise addition of phenylacetyl chloride (3.09 g, 20 mmol) over 1 hour. The reaction mixture was then warmed to room temperature over 2 h, then concentrated *in vacuo*. The residue was dissolved in ethyl acetate (200 mL) and washed with water (2 x 50 mL) then brine (50 mL). The organic layer was then dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo* to yield the intermediate allyl ester (3.57 g, 20 mmol, 100%) as a colorless oil, which was used without further purification in the subsequent diazo transfer reaction. Data for allyl phenylacetate: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.38 – 7.20 (comp, 5 H), 5.89 (ddt, *J* = 17.2, 10.6, 5.7 Hz, 1 H), 5.25 (dq, *J* = 17.2, 1.3 Hz, 1 H), 5.19 (dq, *J* = 10.6, 1.3 Hz, 1 H), 4.59 (dt, *J* = 5.7, 1.3 Hz, 1 H), 3.64 (s, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 171.1, 133.9, 132.0, 129.2, 128.5, 127.1, 118.1, 65.4, 61.3.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (1.82 g, 12 mmol) in THF (10 mL) was added to a solution of allyl phenylacetate (2.0 g, 11.4 mmol) and *p*-acetamidobenzenesulfonyl azide (ABSA) (2.9 g, 12.0 mmol) in anhydrous THF (20 mL) over 1 hour at room temperature.[12] The reaction mixture was stirred for a further 11 hours, then quenched by addition of saturated aqueous ammonium chloride (30 mL). The aqueous layer was extracted with ethyl acetate (2 x 50 mL). The combined organic layers were washed with water (2 x 50 mL) and brine (50 mL), then dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel eluting with 10 % ethyl acetate in hexanes to furnish allyl phenyldiazoacetate **10** (1.7 g, 8.4 mmol, 74 %) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.5 Hz, 2 H), 7.39 (dd, *J* = 8.5, 7.4 Hz, 2 H),

[12] Davies, H. M. L.; Huby, N. J. S.; Cantrell, Jr., W. R.; Olive, J. L. *J. Am. Chem. Soc.*, **1993**, 115, 9468-9479.

7.18 (t, J = 7.4 Hz, 1 H), 5.98 (ddt, J = 17.2, 10.4, 5.7 Hz, 1 H), 5.36 (dq, J = 17.2, 1.5 Hz, 1 H), 5.27 (dq, J = 10.4, 1.5 Hz, 1 H), 4.77 (dt, J = 5.7, 1.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 132.1, 128.9, 125.4, 124.0, 65.4; IR ($CHCl_3$): 2089 (C=N_2), 1699 (C=O); MS (FAB^+): 203.1 (M^++1).

Cyclopropanation of Allyl Phenyldiazoacetate. General Procedure. A solution of allyl phenyldiazoacetate **10** (81 mg, 0.4 mmol) in dichloromethane (CH_2Cl_2) (2 mL) was added *via* syringe pump (1.0 mL/hr) over 2 hours to a refluxing solution of Rh_2(4*S*-MEAZ)$_4$ (2.8 mg, 1.0 mol %) in CH_2Cl_2 (4 mL). After complete addition the reaction mixture was stirred at reflux for a further 30 minutes to ensure complete reaction. The mixture was then cooled to room temperature, then passed through a short silica plug, which was subsequently washed with CH_2Cl_2 (40 mL). The crude product was purifed by flash column chromatography on silica gel eluting with 10 % ethyl acetate in hexanes to furnish the desired cyclopropane **11** (55 mg, 0.32 mmol, 80 %) as a colorless oil, 68 % ee (determined by GC on a 30-m Chiraldex B-DM column, 100°C for 5 min, then 1°C/min to 160°C, $t_{R\ minor}$ = 70.9 min, $t_{R\ major}$ = 72.0 min). Data for **11** : ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.48 – 7.20 (comp, 5H), 4.30 (dd, J = 9.2, 4.6 Hz, 1 H), 4.25 (d, J = 9.2 Hz, 1 H), 2.54 (dt, J = 7.7, 4.6 Hz, 1 H), 1.62 (dd, J = 7.7, 4.6 Hz, 1 H), 1.33 (t, J = 4.6 Hz, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 175.9, 134.0, 128.4, 128.2, 127.5, 67.9, 31.5, 24.9, 19.9; IR ($CHCl_3$): 1765 (C=O); HRMS: Calcd for $C_{11}H_{11}O_2$: 175.0759. Found: 175. 0752.

Synthesis of 2-Methyl-2-buten-l-yl Phenyldiazoacetate (15). Treatment of (2-methyl) allyl alcohol (1.17 g, 16.2 mmol) in CH_2Cl_2 (5 mL) with Et_3N (1.52 g, 15 mmol) and phenylacetyl chloride (1.16 g, 7.5 mmol) as described for the synthesis of **10** (reaction mixture stirred for 16 hours after complete addition of chloride) furnished 2-methyl-2-buten-l-yl phenylacetate (1.2 g, 13.7 mmol, 85 %) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.24 (comp, 5 H), 4.91 (s, 3 H), 4.89 (s, 1 H), 4.51 (s, 2 H), 3.60 (s, 2 H), 1.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 139.7, 133.9, 129.2, 128.5, 127.1, 112.8, 70.0, 41.4, 19.4. Treatment of the intermediate ester (0.90 g, 4.7 mmol) with ABSA (2.66 g, 11.0 mmol), and DBU (1.82 g, 12.0 mmol) in THF (20 + 10 mL) at 50°C overnight furnished diazoacetate **15** (0.25 g, 1.1 mmol, 24 %) as a brown oil, after purification by chromatography on silica

gel, eluting with hexanes: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 2 H), 7.38 (t, *J* = 7.5 Hz, 2 H), 7.17 (t, *J* = 7.5 Hz, 1 H), 5.01 (s, 3 H), 4.96 (s, 1 H), 4.69 (s, 2 H), 1.79 (s, 3 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 164.7, 139.7, 128.9, 125.8, 125.4, 123.9, 123.0, 67.9, 19.4; IR (neat): 2088 (C=N_2), 1692 (C=O); HRMS: Calcd for $C_{12}H_{13}O_2N_2$: 217.0977. Found : 217.0977.

Cyclopropanation of 2-Methyl-2-buten-l-yl Phenyldiazoacetate. Procedure. A solution of 2-methyl-2-buten-l-yl phenyldiazoacetate **15** (43.2 mg, 0.2 mmol) in dichloromethane (CH_2Cl_2) (2 mL) was added *via* syringe pump (1.0 mL/hr) over 2 hours to a refluxing solution of Rh_2(4*S*-MEAZ)$_4$ (1.4 mg, 1.0 mol %) in CH_2Cl_2 (4 mL). After complete addition the reaction mixture was stirred at reflux for a further 30 minutes to ensure complete reaction. The mixture was then cooled to room temperature, then passed through a short silica plug, which was subsequently washed with CH_2Cl_2 (40 mL). Removal of solvent at reduced pressure furnished the desired cyclopropane **16** (31 mg, 0.16 mmol, 82 %) as a solid, 84 % ee (determined by GC on a 30-m Chiraldex B-DM column, 100°C for 5 min, then 1°C/min to 170°C, $t_{R\ minor}$ = 67.7 min, $t_{R\ major}$ = 69.4 min). After one recrystallization from hexanes (5 mL), ee = >99% (59 % yield, 0.12 mmol, 22 mg). Data for **16**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.23 (comp, 5H), 4.34 (d, *J* = 9.0 Hz, 1 H), 4.17 (d, *J* = 9.0 Hz, 1 H), 1.60 (d, *J* = 4.5 Hz, 1 H), 1.37 (d, J = 4.5 Hz, 1 H), 1.15 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 132.0, 130.1, 128.6, 127.9, 73.0, 36.8, 31.1, 22.6, 15.1; IR ($CHCl_3$): 1764 (C=O); m.p. 92.5 - 93°C; $[\alpha]_D^{19}$ +84.0 (*c* 0.64, CH_2Cl_2); HRMS (FAB$^+$) Calcd for $C_{12}H_{13}O_2$: 189.0916. Found: 189.0913.

Synthesis of 3-Methyl-2-buten-l-yl Phenyldiazoacetate (17). Treatment of (3-methyl-2-buten-1-ol (10 mL) with Et_3N (3.09 g, 30 mmol) and phenylacetyl chloride (3.09 g, 20 mmol) as described for the synthesis of **10** furnished the 3-methyl-2-buten-l-yl phenylacetate (4.0 g, 19.6 mmol, 98 %) as a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.33 – 7.20 (comp, 5 H), 5.33 (t, *J* = 7.3 Hz, 1 H), 4.58 (d, *J* = 7.3 Hz, 2 H), 3.60 (s, 2 H), 1.74 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 171.4, 139.0, 134.0, 129.1, 128.4, 126.9, 118.4, 63.6, 41.2, 25.6, 17.9. Treatment of the intermediate ester (1.90 g, 9.3 mmol) with ABSA (2.66 g, 11.0 mmol), and DBU (1.82 g, 12.0 mmol) in THF (20 + 10 mL) furnished diazoacetate **17** (1.29 g, 5.2 mmol, 56 %) as a brown oil, after purification by chromatography on silica

gel, eluting with hexanes: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.50 – 7.11 (comp, 5 H), 5.38 (t sept, *J* = 7.2, 1.4 Hz, 1 H), 4.76 (d, *J* = 7.2 Hz, 2 H), 1.76 (s, 3 H), 1.74 (s, 3 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 165.1, 139.1, 128.8, 125.6, 123.8, 118.6, 61.7, 25.7, 18.0; IR ($CHCl_3$): 2089 (C=N_2), 1692 (C=O); HRMS (FAB$^+$): Calcd. for $C_{13}H_{15}O_2N_2$: 231.1134. Found : 231.1140.

Cyclopropanation of 3-Methyl-2-buten-l-yl Phenyldiazoacetate. Procedure. A solution of 3-methyl-2-buten-l-yl phenyldiazoacetate **17** (92 mg, 0.4 mmol) in dichloromethane (CH_2Cl_2) (2 mL) was added *via* syringe pump (1.0 mL/hr) over 2 hours to a refluxing solution of Rh_2(4*S*-MEAZ)$_4$ (2.8 mg, 1.0 mol %) in CH_2Cl_2 (4 mL). After complete addition the reaction mixture was stirred at reflux for a further 30 minutes to ensure complete reaction. The mixture was then cooled to room temperature, then passed through a short silica plug, which was subsequently washed with CH_2Cl_2 (40 mL). The crude product was purifed by flash column chromatography on silica gel eluting with CH_2Cl_2 to furnish the desired cyclopropane **18** (75 mg, 0.36 mmol, 92 %) as a colorless oil, 19 % ee (determined by GC on a 30-m Chiraldex B-DM column, 100°C for 5 min, then 1°C/min to 175°C, $t_{R\ major}$ = 71.2 min, $t_{R\ minor}$ = 71.7 min). Data for **18** : ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.38 – 7.25 (comp, 5H), 4.50 (dd, *J* = 9.8, 5.3 Hz, 1 H), 4.24 (d, *J* = 9.8 Hz, 1 H), 2.39 (d, *J* = 5.3 Hz, 1 H), 1.30 (s, 3 H), 0.86 (s, 3 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 174.9, 132.7, 129.6, 128.3, 127.6, 65.3, 41.9, 33.0, 27.5, 22.6, 15.6; IR ($CHCl_3$): 1757 (C=O); HRMS: Calcd for $C_{12}H_{15}O_2$: 203.1072. Found: 203.1069.