Supporting Information

For

**A Highly Efficient and Selective Route to
Isomeric Cyclic Diazadienes**

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General

Melting points were recorded using a Fisher-Johns melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded using either a Varian Mercury 400 MHz or Varian Unity 500 MHz spectrometer in CDCl_3 with chemical shifts relative to tetramethylsilane (TMS, 0 ppm) unless otherwise reported. No special notation is used for equivalent carbons. IR spectra were obtained using a Nicolet DX FT IR spectrometer as thin films on NaCl plates. High-resolution mass spectra were obtained using either a VG 70-250S (double focusing) mass spectrometer at 70 eV or a Sciex Qstar turbo ionspray mass spectrometer.

Diethyl ether and dichloromethane were dried and degassed using an MBRAUN MB solvent purification system. Tetrahydrofuran (THF) was distilled from Na/benzophenone prior to use. Dimethoxyethane was distilled from CaH_2 prior to use. All other reagents were used as received unless otherwise indicated. MgI_2 was weighed out in a glovebox to prevent the absorption of water. Neutral silica (Silicycle, Quebec, Canada) for flash chromatography was used as received. All experiments were performed under anhydrous conditions under an atmosphere of argon. 2-Methylene-cyclopropanecarboxylic acid,¹ dideuteriodiiodomethane² and buta-2,3-dien-1-ol³ were prepared as previously reported.

Starting Material Synthesis

2-Methylene-cyclopropanecarboxylic acid methoxy-methyl-amide

To a solution of 2-methylene-cyclopropanecarboxylic acid (7.16 g, 73.0 mmol) in dichloromethane (372 mL) at 0 °C was added carbonyldiimidazole (14.1 g, 87.1 mmol). The resulting solution was stirred for 1 hour at 0 °C. To this solution was added *O,N*-dimethylhydroxylamine hydrochloride (17.8 g, 0.183 mol) and the reaction was stirred overnight. The reaction solution was then filtered through a bed of Celite[®] and the filtrate was concentrated *in vacuo*. Flash chromatography on silica using 2:3 diethyl ether:hexanes (R_f = 0.21) afforded the title compound (8.96 g, 87%) as a colourless oil. IR (neat, cm^{-1}) 3565, 2975, 2938, 1654, 1458, 1418, 1385, 1179, 1110, 988, 908, 890, 736, 686; δ_{H} (400 MHz, CDCl_3) 5.45 (m, 1H), 5.41 (m, 1H), 3.78 (s, 3H), 3.23 (s, 3H), 2.80 (m, 1H), 1.88 (m, 1H), 1.60 (apparent tt, 1H, J = 8.6, 2.4 Hz); δ_{C} (100 MHz, CDCl_3) 171.9, 131.7, 104.0, 61.9, 32.8, 16.0, 10.6; $\text{C}_7\text{H}_{11}\text{NO}_2$ (M^+) (EI) Requires: 141.0790 Found: 141.0793.

1-(2-Methylene-cyclopropyl)-ethanone-tosyl-hydrazone

To a solution of 2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.268 g, 1.90 mmol) in diethyl ether (10.3 mL) at -78°C was added a solution of MeMgBr in diethyl ether (3.2 M, 0.66 mL, 2.11 mmol). The resulting white suspension was then stirred to room temperature for 4 hours until the reaction was complete. To this solution was added a 1 N HCl solution (10 mL). The reaction solution was then extracted with diethyl ether (4×50 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The crude product was then taken up in dichloromethane (9.5 mL, 0.2 M) and Na_2SO_4 and *p*-tosylhydrazine (0.355 g, 1.91 mmol) were added. The resulting solution was stirred at room temperature overnight and was then filtered and concentrated *in vacuo*. Flash chromatography on silica using 1:2 ethyl acetate:hexanes ($R_f = 0.47$) afforded the title compound (0.375 g, 75%) as a white solid and as a 3:1 mixture of isomers. IR (neat, cm^{-1}) 3216, 2988, 1620, 1598, 1396, 1337, 1314, 1166, 1091, 1059, 1018, 900, 815, 682; δ_{H} (400 MHz, CDCl_3) 7.87 (d, 1.5H, $J = 8.1$ Hz), 7.86 (d, 0.5H, $J = 8.1$ Hz), 7.75 (bs, 1H), 7.37 (bs, 1H), 7.32 (d, 2H, $J = 8.3$ Hz), 5.53 (m, 0.25H), 5.51 (m, 0.75H), 5.48 (m, 0.25H), 5.45 (m, 0.75H), 2.44 (s, 3H), 2.39 (m, 0.75H), 2.28 (m, 0.25H), 1.70 (s, 0.75H), 1.69 (m, 0.25H), 1.50 (m, 0.75H), 1.50 (s, 3H), 1.32 (m, 1H); δ_{C} (125 MHz, CDCl_3) 157.8, 157.7, 144.8, 144.2, 135.7, 133.8, 131.7, 131.6, 130.2, 129.9, 129.7, 128.5, 128.4, 128.3, 106.4, 106.1, 104.7, 27.8, 27.3, 23.2, 21.8, 19.8, 15.5, 12.6, 11.6, 10.4, 9.6; $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ (M^+) (EI) Requires: 264.0933 Found: 264.0937.

1-(2-Methylene-cyclopropyl)-propan-1-one-tosyl-hydrazone

To a solution of 2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.228 g, 1.62 mmol) in diethyl ether (9.6 mL) at -78°C was added a solution of EtMgCl in diethyl ether (3.0 M, 0.80 mL, 2.40 mmol). The resulting white suspension was stirred at room temperature for 7 hours until the reaction was complete. To this solution was added a 1 N HCl solution (10 mL). The reaction solution was then extracted with diethyl ether (4×50 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The crude product was taken up in dichloromethane (8.1 mL, 0.2 M) and Na_2SO_4 and *p*-tosylhydrazine (0.452 g, 2.42 mmol) were added. The resulting solution was stirred at room temperature for one week and was then filtered and concentrated *in vacuo*. Flash chromatography on silica using 1:2 ethyl acetate:hexanes ($R_f = 0.6$ -0.5) afforded the title compound (0.390 g, 87% over two steps) as a white solid and as a 1.9:1 mixture of isomers. IR (neat, cm^{-1}) 3216, 2977, 1620, 1598, 1454, 1402, 1330, 1165, 1091, 1020, 890, 814, 668; δ_{H} (400 MHz, CDCl_3) 7.86 (d, 1.3H, $J = 8.6$ Hz), 7.84 (d, 0.7H, $J = 8.6$ Hz), 7.74 (bs, 0.65H), 7.40 (bs, 0.35H), 7.31 (d, 2H, $J = 7.8$ Hz), 5.53 (m, 0.65H), 5.50 (m, 0.65H), 5.47 (m, 0.35H), 5.42 (m, 0.35H), 2.43 (s, 3H), 2.30 (m, 0.35H), 2.15 (m, 0.65H), 2.10-1.84 (m, 2H), 1.67 (apparent tt, 0.65H, $J = 9.2, 2.3$ Hz), 1.48 (apparent tt, 0.35H, $J = 9.2, 2.3$ Hz), 1.40 (m, 0.35H), 1.22 (m, 0.65H), 1.01 (t, 1.05H, $J = 7.8$ Hz), 0.98 (t, 1.95H, $J = 7.4$ Hz); δ_{C} (100 MHz, CDCl_3) 161.2, 159.6, 144.1, 135.6, 131.9, 129.7, 129.6, 128.3,

128.3, 106.3, 105.5, 27.1, 21.8, 21.8, 20.1, 14.8, 10.7, 10.4, 10.1, 9.6; C₁₄H₁₉N₂O₂S (MH⁺) (ESI) Requires: 279.1161 Found: 279.1150.

1-(2-Methylene-cyclopropyl)-2-phenyl-ethanone-tosyl-hydrazone

To a solution of 2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.125 g, 0.885 mmol) in diethyl ether (4.8 mL) at -78 °C was added a solution of BnMgBr in diethyl ether (0.6 M, 1.62 mL, 0.972 mmol). The resulting solution was then stirred to room temperature for 1.5 days. To this solution was added a 1 N HCl solution (10 mL). The reaction solution was extracted with diethyl ether (4×50 mL) and the combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was taken up in dichloromethane (4.5 mL, 0.2 M) and Na₂SO₄ and *p*-tosylhydrazine (0.248 g, 1.33 mmol) were added. The resulting solution was stirred at room temperature for 7 days and was then filtered and concentrated *in vacuo*. Flash chromatography on silica using 15:85→1:2 ethyl acetate:hexanes (*R_f* = 0.53 in 1:2 ethyl acetate:hexanes) afforded the title compound (0.209 g, 69% over two steps) as a white solid and as a 1:1 mixture of isomers. IR (neat, cm⁻¹) 3218, 3027, 1598, 1494, 1454, 1397, 1334, 1166, 1092, 1031, 889, 813, 728, 703, 669; δ_H (400 MHz, CDCl₃) 7.99 (bs, 1H), 7.81 (d, 1H, *J* = 8.6 Hz), 7.63 (d, 1H, *J* = 8.2 Hz), 7.32-7.14 (m, 5H), 6.92 (m, 2H), 5.49 (m, 0.5H), 5.46 (m, 0.5H), 5.37 (m, 1H), 3.36 (s, 1H), 3.30 (AB, 0.5H, *J* = 16.4 Hz), 3.27 (AB, 0.5H, *J* = 16.4 Hz), 2.46 (s, 1.5H), 2.45 (s, 1.5H), 2.08 (m, 0.5H), 1.61 (m, 0.5H), 1.60 (apparent tt, 0.5H, *J* = 9.4, 2.3 Hz), 1.52 (apparent tt, 0.5H, *J* = 9.0, 2.0 Hz), 1.35 (m, 0.5H), 1.14 (m, 0.5H); δ_C (100 MHz, CDCl₃) 157.7, 156.8, 144.2, 144.1, 136.8, 135.5, 135.4, 133.7, 131.4, 129.7, 129.6, 129.5, 128.9, 128.4, 128.3, 128.2, 127.9, 127.5, 126.7, 106.9, 106.1, 40.6, 32.4, 22.9, 21.8, 14.8, 10.6, 9.6; C₁₉H₂₁N₂O₂S (MH⁺) (ESI) Requires: 341.1324 Found: 341.1324.

1-(2-Methylene-cyclopropyl)-pentan-1-one-tosyl-hydrazone

To a solution of 2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.200 g, 1.42 mmol) in diethyl ether (7.7 mL) at -78 °C was added a solution of BuLi in hexanes (1.6 M, 0.98 mL, 1.57 mmol). The resulting solution was stirred to room temperature for 4 hours until the reaction was complete. To this solution was added a 1 N HCl solution (10 mL). The reaction solution was extracted with diethyl ether (4×50 mL) and the combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was then taken up in dichloromethane (7.1 mL, 0.2 M) and Na₂SO₄ and *p*-tosylhydrazine (0.397 g, 2.13 mmol) were added. The resulting solution was stirred at room temperature for 4 days and was then filtered and concentrated *in vacuo*. Flash chromatography on silica using 1:2 ethyl acetate:hexanes (*R_f* = 0.38) afforded the title compound (0.364 g, 88% over two steps) as a white solid and as a 1.1:1 mixture of isomers. IR (neat, cm⁻¹) 3116, 2971, 1598, 1455, 1392, 1330,

1165, 1093, 1019, 894, 812, 666; δ_H (400 MHz, $CDCl_3$) 7.89 (bs, 0.54H), 7.85 & 7.83 (2×d, 2H, 2× J = 8.2 Hz), 7.52 (bs, 0.46H), 7.31 (d, 2H, J = 7.8 Hz), 5.52 (m, 0.54H), 5.50 (m, 0.54H), 5.45 (s, 0.46H), 5.39 (s, 0.46H), 2.43 (s, 3H), 2.27 & 2.14 (m, 1H), 2.05-1.80 (m, 2H), 1.68 (apparent tt, 0.54H, J = 9.0, 2.3 Hz), 1.49-1.10 (m, 5.46H), 0.87-0.80 (m, 3H); δ_C (100 MHz, $CDCl_3$) 160.4, 158.7, 144.1, 135.7, 135.5, 132.1, 129.6, 129.6, 128.3, 106.3, 105.2, 33.5, 28.5, 27.9, 27.2, 23.0, 22.3, 22.0, 21.8, 21.8, 14.8, 14.1, 13.9, 10.1, 9.7; $C_{16}H_{23}N_2O_2S$ (MH^+) (ESI) Requires: 307.1474 Found: 307.1479.

1-(2-Methylene-cyclopropyl)-but-3-en-1-one-tosyl-hydrazone

To a solution of 2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.200 g, 1.42 mmol) in THF (7 mL) at 0 °C was added a solution of allylMgBr in diethyl ether (1.0 M, 4.26 mL, 4.26 mmol). The resulting solution was then stirred to room temperature for 12 hours until the reaction was complete. To this solution was added a 1 N HCl solution (10 mL). The reaction solution was extracted with diethyl ether (4×50 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The crude product was then taken up in absolute ethanol (10 mL, 0.14 M) and molecular sieves and *p*-tosylhydrazine (0.397 g, 2.13 mmol) were added. The resulting solution was stirred at room temperature for 12 hours and was then filtered and concentrated *in vacuo*. Flash chromatography on silica using 1:3 ethyl acetate:hexanes (R_f = 0.21) afforded the title compound (0.150 g, 36% over two steps) as a light yellow solid and as a 1:1 mixture of isomers. IR (neat, cm^{-1}) 3610, 3215, 2921, 1391, 1330, 1163; δ_H (400 MHz, $CDCl_3$) 8.21 (s, 0.5H), 7.85 (d, 1H, J = 6.7 Hz), 7.81 (d, 1H, J = 6.7 Hz), 7.65 (s, 0.5H), 7.31 (d, 1H, J = 3.9 Hz), 7.29 (d, 1H, J = 3.8 Hz), 5.67 (m, 1H), 5.51 (m, 1H), 5.44 (m, 1H), 5.02 (m, 1H), 4.97 (dd, 0.5H, J = 17.1, 1.6 Hz), 4.79 (dd, 0.5H, J = 17.4, 1.2 Hz), 2.76 (m, 0.5H), 2.68 (m, 0.5H), 2.43 (s, 1.5H), 2.42 (s, 1.5H), 2.38 (m, 0.5H), 2.21 (m, 0.5H), 1.69 (m, 0.5H), 1.49 (m, 0.5H), 1.34 (m, 0.5H), 1.26 (m, 1H); δ_C (100 MHz, $CDCl_3$) 157.2, 157.1, 144.19, 144.15, 135.6, 135.5, 133.6, 131.4, 130.4, 129.8, 129.68, 129.67, 128.3, 128.2, 117.8, 117.3, 106.6, 106.1, 38.1, 30.6, 22.5, 21.84, 21.82, 15.0, 10.5, 9.4; $C_{15}H_{19}N_2O_2S$ (MH^+) (ESI) Requires: 291.1161 Found: 291.1162.

4-(tert-Butyl-dimethyl-silanyloxy)-1-(2-methylene-cyclopropyl)-butan-1-one-tosyl-hydrazone

To a solution of 2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.249 g, 1.76 mmol) in THF (9.5 mL) at -78 °C was added a solution of the requisite Grignard reagent in THF (0.40 M, 8.7 mL, 3.48 mmol). The resulting solution was then stirred to room temperature for 10 hours. To this solution was added a 1 N HCl solution (10 mL). The reaction solution was then extracted with diethyl ether (4×50 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The crude product was then purified on silica using 1:9 diethyl ether:hexanes and the resulting ketone was taken up in dichloromethane (8.8 mL, 0.2 M) and Na_2SO_4 and *p*-tosylhydrazine (0.650 g, 3.49 mmol) were added. The

resulting solution was stirred at room temperature for 4.5 days and was then filtered and concentrated *in vacuo*. Flash chromatography on silica using 1:4 diethyl ether:hexanes ($R_f = 0.25-0.14$) afforded the title compound (0.741 g, 99% over two steps) a clear oil as a 1.2:1 mixture of isomers that upon solidifying under high vacuum, was isolated as a white solid and as a 11:1 mixture of isomers.⁴ IR (neat, cm^{-1}) 3216, 2931, 2956, 2739, 2255, 1915, 1799, 1747, 1632, 1599, 1495, 1469, 1392, 1336, 1257, 1168, 1093, 1020, 897, 836, 812, 777, 706, 665; δ_{H} (400 MHz, CDCl_3) 8.78 (s, 0.55H), 8.11 (bs, 0.45H), 7.79 (m, 2H), 7.24 (m, 2H), 5.46 (s, 0.88H), 5.38 (s, 0.56H), 5.30 (s, 0.56H), 3.44 (bs, 0.91H), 3.29 (m, 1.09H), 2.37 (s, 3H), 2.24-1.91 (m, 3H), 1.66-1.50 (m, 2.45H), 1.39 (bs, 1H), 1.21 (m, 0.55H), 0.90 (s, 4.85H), 0.81 (s, 4.15H), 0.08 (s, 3.20H), -0.06 (s, 2.8H); δ_{C} (100 MHz, CDCl_3) 158.5, 157.7, 143.9, 143.5, 136.1, 135.6, 132.4, 129.8, 129.5, 129.3, 128.2, 128.0, 106.1, 104.9, 62.2, 60.8, 29.5, 29.1, 28.9, 26.1, 26.0, 23.1, 22.0, 21.7, 18.5, 18.4, 15.0, 10.2, 9.5, -5.0, -5.3; $\text{C}_{21}\text{H}_{35}\text{N}_2\text{O}_3\text{SSi}$ (MH^+) (ESI) Requires: 423.2132 Found: 423.2132.

[1,3]-Dithian-2-yl-(2-methylene-cyclopropyl)-methanone-tosyl-hydrazone

The Grignard solution was prepared by the dropwise addition of BuLi in hexanes (1.6 M, 1.8 mL, 2.88 mmol) to a solution of 1,3-dithiane (0.340 g, 2.83 mmol) in THF (30 mL) at $-78\text{ }^{\circ}\text{C}$. The solution was stirred to $-40\text{ }^{\circ}\text{C}$ for 1 hour before being cooled back down to $-78\text{ }^{\circ}\text{C}$ prior to the addition of 2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.184 g, 1.30 mmol) in THF (8 mL). The resulting solution was then stirred to room temperature overnight. The reaction solution was quenched by the addition of water (20 mL), followed by extraction with diethyl ether ($4 \times 50\text{ mL}$). The combined organic layers were then washed with brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The crude product was purified on silica from excess 1,3-dithiane using 1:4 diethyl ether:hexanes to afford the ketone product which was subsequently taken up in dichloromethane (14.4 mL, 0.2 M) and Na_2SO_4 and *p*-tosylhydrazine (0.484 g, 2.60 mmol) were added. *p*-Toluene sulfonic acid monohydrate (0.0247 g, 10 mol%) was then added in order to the reaction to proceed. The resulting solution was stirred at room temperature for 8 days and was then filtered and concentrated *in vacuo*. Flash chromatography on silica using 15:85 ethyl acetate:hexanes ($R_f = 0.13$) afforded the title compound (0.150 g, 31% over two steps) as a white solid and as a single isomer, mp = $134-137\text{ }^{\circ}\text{C}$ (CH_2Cl_2). IR (neat, cm^{-1}) 3214, 2927, 1397, 1335, 1159; δ_{H} (400 MHz, CDCl_3) 8.40 (s, 1H), 7.89 (d, 2H, $J = 8.2\text{ Hz}$), 7.32 (d, 2H, $J = 8.1\text{ Hz}$), 5.66 (m, 1H), 5.57 (m, 1H), 4.16 (s, 1H), 3.09 (m, 1H), 2.96 (m, 1H), 2.58 (m, 2H), 2.42 (s, 3H), 2.19 (m, 1H), 1.95 (m, 2H), 1.79 (m, 1H), 1.26 (m, 1H); δ_{C} (100 MHz, CDCl_3) 154.2, 144.4, 135.4, 129.8, 129.0, 128.3, 107.3, 45.0, 27.8, 25.7, 21.9, 13.9, 11.1; $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}_2\text{S}_3$ (M^+) (ESI) Requires: 369.0759 Found: 369.0751.

(2-Methylene-cyclopropyl)-phenyl-methanone-tosyl-hydrazone

To a solution of 2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.210 g, 1.48 mmol) in diethyl ether (8.1 mL) at $-78\text{ }^{\circ}\text{C}$ was added a solution of PhMgBr in diethyl ether (2.5 M, 1.3 mL, 3.25 mmol). The resulting solution was then stirred to room temperature overnight. To this solution was added a 1 N HCl solution (10 mL). The reaction solution was then extracted with diethyl ether (4×50 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The crude product was then taken up in dichloromethane (7.4 mL, 0.2 M) and Na_2SO_4 , *p*-tosylhydrazine (0.551 g, 2.96 mmol) and *p*-toluene sulfonic acid monohydrate (0.0282 g, 10 mol%) were added. The resulting solution was stirred at room temperature for 6 days and was then filtered and concentrated *in vacuo*. Flash chromatography on silica using 15:85 ethyl acetate:hexanes ($R_f = 0.21$) afforded the title compound (0.357 g, 74% over two steps) as a white solid and as a 2.3:1 mixture of isomers. IR (neat, cm^{-1}) 3213, 2926, 1598, 1440, 1383, 1323, 1344, 1305, 1167, 1089, 1015, 895, 814, 768, 666; δ_{H} (400 MHz, CDCl_3) 8.41 (bs, 0.60H), 7.88 (d, 1.2H, $J = 8.2$ Hz), 7.78 (d, 0.8H, $J = 8.2$ Hz), 7.61 (dd, 1.2H, $J = 6.6, 3.1$ Hz), 7.40 (m, 1.2H), 7.33 (m, 3.8H), 7.23 (bs, 0.4H), 7.00 (dd, 0.8H, $J = 6.6, 2.7$ Hz), 5.62 (m, 0.6H), 5.58 (m, 0.6H), 5.46 (m, 0.4H), 5.40 (m, 0.4H), 2.54 (m, 0.4H), 2.45 (s, 1.2H), 2.41 (s, 1.8H), 2.34 (dddd, 0.6H, $J = 8.8, 6.2, 2.5, 2.3$ Hz), 1.84 (apparent tt, 0.6H, $J = 9.0, 2.3$ Hz), 1.49 (m, 0.4H), 1.21 (m, 1H); δ_{C} (100 MHz, CDCl_3) 157.5, 151.8, 144.4, 144.2, 136.2, 135.7, 131.6, 130.4, 130.1, 129.8, 129.8, 129.7, 129.6, 129.5, 128.7, 128.3, 128.2, 128.1, 127.7, 127.6, 125.6, 107.2, 106.0, 22.8, 21.9, 21.8, 13.8, 10.6, 9.9; $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$ (MH^+) (ESI) Requires: 327.1161 Found: 327.1163.

Furan-2-yl-(2-methylene-cyclopropyl)-methanone-tosyl-hydrazone

The Grignard solution was prepared by the dropwise addition of BuLi in hexanes (1.6 M, 1.8 mL, 2.88 mmol) to a solution of furan (0.200 g, 2.94 mmol) in THF (31 mL) at $-78\text{ }^{\circ}\text{C}$. The solution was stirred to $-40\text{ }^{\circ}\text{C}$ for 45 minutes before being cooled back down to $-78\text{ }^{\circ}\text{C}$ prior to the addition of 2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.192 g, 1.36 mmol) in THF (8 mL). The resulting solution was stirred to room temperature overnight. The reaction solution was quenched by the addition of water (20 mL), followed by extraction with diethyl ether (4×50 mL). The combined organic layers were then washed with brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The crude product was purified on silica using 1:4 diethyl ether:hexanes to afford the ketone product which was subsequently taken up in dichloromethane (14.4 mL, 0.2 M) and Na_2SO_4 , *p*-tosylhydrazine (0.505 g, 2.71 mmol), and *p*-toluene sulfonic acid monohydrate (0.0257 g, 10 mol%) were added. The resulting solution was stirred at room temperature for 8 days and was then filtered and concentrated *in vacuo*. Flash chromatography on silica using 15:85 ethyl acetate:hexanes ($R_f = 0.11$) afforded the title compound (0.190 g, 44% over two steps) as a white solid and as a 2.1:1 mixture of isomers. IR (neat, cm^{-1}) 3613, 2927, 2855, 1746, 1518, 1488, 1162; δ_{H} (400 MHz, CDCl_3) 9.36 (s, 0.68H),

8.57 (s, 0.32H), 7.87 (d, 0.64H, $J = 8.4$ Hz), 7.81 (d, 1.36H, $J = 8.4$ Hz), 7.56 (d, 0.68H, $J = 1.8$ Hz), 7.39 (d, 0.32H, $J = 1.8$ Hz), 7.27 (m, 2H), 6.82 (d, 0.68H, $J = 3.7$ Hz), 6.70 (d, 0.32H, $J = 3.4$ Hz), 6.50 (dd, 0.68H, $J = 3.7, 1.9$ Hz), 6.35 (dd, 0.32H, $J = 3.5, 1.8$ Hz), 5.64 (m, 0.64H), 5.39 (m, 1H, 1.36H), 2.42 (m, 0.68H), 2.38 (s, 2.04H), 2.37 (s, 0.96H), 2.28 (m, 0.32H), 1.82 (m, 0.32H), 1.63 (m, 0.68H), 1.53 (m, 0.68H), 1.41 (m, 0.32H); δ_C (100 MHz, $CDCl_3$) 150.6, 149.0, 144.4, 144.2, 143.9, 143.8, 139.3, 135.6, 132.4, 129.8, 129.6, 128.2, 114.8, 111.9, 111.8, 111.6, 107.4, 104.1, 21.8, 18.9, 13.2, 10.7, 9.8; $C_{16}H_{17}N_2O_3S$ (MH^+) (ESI) Requires: 317.0954 Found: 317.0960.

1-(2-Methylene-cyclopropyl)-ethanone oxime

To a solution of 2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.565 g, 4.00 mmol) in THF (23.7 mL) at $-78^\circ C$ was added a solution of MeMgBr in diethyl ether (3.2 M, 2.0 mL, 6.40 mmol). The resulting white suspension was stirred to room temperature for 4 hours until the reaction was complete. To this solution was added a 1 N HCl solution (10 mL) and the reaction solution was extracted with diethyl ether (4×50 mL). The combined organic layers were then washed with brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo* to afford a crude product that was taken up in a water (3.3 mL)/ethanol (14.3 mL) solution containing sodium acetate (3.37 g, 41.1 mmol) and hydroxylamine hydrochloride (1.02 g, 14.7 mmol). The resulting solution was stirred at room temperature overnight until complete by TLC. Brine was added and the resulting solution was extracted with dichloromethane (4×50 mL). The combined organic layers were then dried with Na_2SO_4 , filtered and concentrated *in vacuo*. Flash chromatography on silica using 1:3 diethyl ether:hexanes ($R_f = 0.25-0.22$) afforded the title compound (0.444 g, 100%) as a clear oil and as a 2.8:1 mixture of isomers. IR (neat, cm^{-1}) 3241, 2922, 1652, 1433, 1370, 1316, 1273, 1116, 1035, 989, 955, 896; δ_H (400 MHz, $CDCl_3$) 9.39 (bs, 1H), 5.56 (m, 0.74H), 5.53 (m, 1H), 5.50 (m, 0.26H), 3.17 (m, 0.26H), 2.34 (m, 0.74H), 1.69 (s, 2.22H), 1.67 (apparent tt, 0.74H, $J = 9.4, 2.3$ Hz), 1.59 (s, 0.78H), 1.54 (apparent tt, 0.26H, $J = 9.2, 2.1$ Hz), 1.45 (m, 0.26H), 1.35 (m, 0.74H); δ_C (125 MHz, $CDCl_3$) 158.0, 157.2, 131.8, 131.4, 106.1, 105.5, 20.3, 14.9, 14.3, 10.2, 9.8, 9.4; C_6H_8NO ($M-H^+$) (EI) Requires: 94.0657 Found: 94.0660.

General Procedure for the Dienamine

To a sealed oven-dried vial purged with argon, was added the MCP hydrazone followed by DME (0.01 M) and TMEDA (redistilled, 1 equivalent) under a cone of argon with stirring. $MgCl_2$ (10 mol%) was then added and the vial was immediately sealed and heated at $120^\circ C$ until the reaction was judged complete by TLC. The resulting solution was evaporated and loaded directly onto the silica column and purified by flash chromatography to afford the title compound in the indicated yield.

3,5-Dimethyl-1-(toluene-4-sulfonyl)-1,2-dihydro-pyridazine

According to the general procedure outlined above using 1-(2-methylene-cyclopropyl)-ethanone-tosyl-hydrazone (0.0200 g, 0.0757 mmol), TMEDA (11.3 μ L, 0.0754 mmol) and MgCl_2 (0.7 mg, 10 mol%) in DME (7.5 mL) at 120 $^\circ\text{C}$ for 3.5 hours, the title compound could be obtained after flash chromatography on silica using 1:4 ethyl acetate:hexanes (R_f = 0.26 in 25% ethyl acetate in hexanes) in 85% yield (0.0170 g) and with a selectivity of > 20:1 over the azadiene product. White solid. IR (neat, cm^{-1}) 3240, 2925, 1597, 1441, 1347, 1186, 1166, 1091, 813, 716, 666; δ_{H} (500 MHz, CDCl_3) 7.65 (d, 2H, J = 8.3 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.01 (bs, 1H), 5.99 (s, 1H), 5.60 (s, 1H), 2.46 (s, 3H), 1.92 (s, 3H), 1.88 (s, 3H); δ_{C} (125 MHz, CDCl_3) 145.2, 134.6, 130.5, 130.0, 128.7, 118.0, 117.6, 107.5, 21.9, 12.1, 10.9; $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$ (MH^+) (ESI) Requires: 265.1005 Found: 265.0998.

3-Ethyl-5-methyl-1-(toluene-4-sulfonyl)-1,2-dihydro-pyridazine

According to the general procedure outlined above using 1-(2-methylene-cyclopropyl)-propan-1-one-tosyl-hydrazone (0.0150 g, 0.0539 mmol), TMEDA (8.1 μ L, 0.0540 mmol) and MgCl_2 (0.5 mg, 10 mol%) in DME (5.4 mL) at 120 $^\circ\text{C}$ for 4 hours, the title compound could be obtained after flash chromatography on silica using 16:84 diethyl ether:hexanes (R_f = 0.23 in ethyl acetate/hexanes 1:3) in 77% combined yield (0.0110 g of dienamine) and with a selectivity of > 20:1 over the azadiene product. Colorless oil. IR (film, cm^{-1}) 3229, 2963, 2927, 1593, 1440, 1344; δ_{H} (400 MHz, CDCl_3) 7.67 (d, 2H, J = 8.2 Hz), 7.31 (d, 2H, J = 8.6 Hz), 6.89 (s, 1H), 5.95 (s, 1H), 5.63 (s, 1H), 2.46 (s, 3H), 2.27 (q, 2H, J = 7.41 Hz), 1.93, (s, 3H), 1.06 (t, 3H, J = 7.41 Hz); δ_{C} (100 MHz, CDCl_3) 145.2, 136.9, 134.6, 130.0, 128.7, 117.9, 117.7, 105.8, 21.9, 18.3, 12.7, 12.2; $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ (M^+) (EI) Requires: 278.1089 Found: 278.1083.

3-Benzyl-5-methyl-1-(toluene-4-sulfonyl)-1,2-dihydro-pyridazine

According to the general procedure outlined above using 1-(2-methylene-cyclopropyl)-2-phenyl-ethanone-tosyl-hydrazone (0.0150 g, 0.0441 mmol), TMEDA (7.1 μ L, 0.0474 mmol) and MgCl_2 (0.4 mg, 10 mol%) in DME (4.5 mL) at 120 $^\circ\text{C}$ for 4 hours, the title compound could be obtained after flash chromatography on silica using 16:84 diethyl ether:hexanes (R_f = 0.32 in 1:3 ethyl acetate:hexanes) in 70% combined yield (0.0095 g of dienamine) and with a selectivity of 10:1 over the azadiene product. Colorless oil. IR (neat, cm^{-1}) 3242, 2921, 1494, 1337, 1164, 1089; δ_{H} (400 MHz, CDCl_3) 7.67 (d, 2H, J = 8.22 Hz), 7.31 (d, 2H, J = 8.0 Hz), 7.24 (m, 2H), 7.17 (m, 1H), 7.03 (d, 2H, J = 7.24 Hz), 6.80 (s, 1H), 6.03 (bs, 1H), 5.54 (s, 1H), 3.52 (s, 2H), 2.46 (s,

3H), 1.91 (s, 3H); δ_C (100 MHz, $CDCl_3$) 145.3, 138.9, 134.7, 133.2, 130.1, 128.9, 128.7, 128.6, 126.5, 118.8, 117.6, 108.6, 31.7, 21.9, 12.2; $C_{19}H_{20}N_2O_2S$ (M^+) (EI) Requires: 340.1246 Found: 340.1237.

Additionally, the reaction could be carried out under higher concentration (0.028 M) using 1-(2-methylene-cyclopropyl)-2-phenyl-ethanone-tosyl-hydrazone (0.0512 g, 0.150 mmol), TMEDA (23 μ L, 0.153 mmol) and $MgCl_2$ (1.4 mg, 10 mol%) in DME (5.4 mL) at 120 °C for 5 hours. The title compound could be obtained after flash chromatography on silica using 16:84 diethyl ether:hexanes (R_f = 0.32 in 1:3 ethyl acetate:hexanes) in 74% combined yield (0.0345 g of dienamine) and with a selectivity of 10:1 over the azadiene product.

3-Butyl-5-methyl-1-(toluene-4-sulfonyl)-1,2-dihydro-pyridazine

According to the general procedure outlined above using 1-(2-methylene-cyclopropyl)-pentan-1-one-tosyl-hydrazone (0.0150 g, 0.0490 mmol), TMEDA (7.4 μ L, 0.0494 mmol) and $MgCl_2$ (0.5 mg, 10 mol%) in DME (4.5 mL) at 120 °C for 4 hours, the title compound could be obtained after flash chromatography on silica using 16:84 diethyl ether:hexanes (R_f = 0.34 in ethyl acetate/hexanes 1:3) in 91% combined yield (0.0132 g of dienamine) and with a selectivity of > 20:1 over the azadiene product. Colorless oil. IR (neat, cm^{-1}) 3611, 2921, 2860, 1701, 1521, 1167; δ_H (400 MHz, $CDCl_3$) 7.67 (d, 2H, J = 6.63 Hz), 7.31 (d, 2H, J = 7.8 Hz), 6.88 (s, 1H), 6.00 (s, 1H), 5.61 (s, 1H), 2.45 (s, 3H), 2.18 (t, 2H, J = 7.4 Hz), 1.93 (s, 3H), 1.40 (m, 2H), 1.26 (m, 2H), 0.85 (t, 3H, J = 7.4 Hz); δ_C (100 MHz, $CDCl_3$) 145.2, 135.4, 134.6, 130.0, 128.7, 117.9, 117.6, 106.3, 30.7, 24.7, 22.7, 21.9, 14.1, 12.2; $C_{16}H_{23}N_2O_2S$ (MH^+) (ESI) Requires: 307.1474 Found: 307.1480.

3-Allyl-5-methyl-1-(toluene-4-sulfonyl)-1,2-dihydro-pyridazine

According to the general procedure outlined above using 1-(2-methylene-cyclopropyl)-but-3-en-1-one-tosyl-hydrazone (0.0165 g, 0.0570 mmol), TMEDA (8.5 μ L, 0.0567 mmol) and $MgCl_2$ (0.5 mg, 10 mol%) in DME (4.5 mL) at 120 °C for 4 hours, the title compound could be obtained after flash chromatography on silica using 7:3 dichloromethane:hexanes (R_f = 0.14) in 87% combined yield (0.0136 g of dienamine) and with a selectivity of > 20:1 over the azadiene product. Colorless oil. IR (neat, cm^{-1}) 3604, 2922, 1698, 1521, 1497, 1160; δ_H (400 MHz, CD_3CN) 8.47 (s, 1H), 7.64 (d, 2H, J = 8.22 Hz), 7.41 (d, 2H, J = 8.41 Hz), 5.82 (m, 1H), 5.80 (s, 1H), 5.59 (s, 1H), 5.01 (m, 1H), 4.98 (m, 1H), 3.08 (d, 2H, J = 6.65 Hz), 2.46 (s, 3H), 1.85 (s,

3H); δ_C (100 MHz, CD_3CN) 160.0, 146.7, 136.7, 136.3, 131.3, 129.5, 119.1, 118.1, 116.8, 108.0, 30.7, 22.0, 12.3; $C_{15}H_{18}N_2O_2S$ (MH^+) (ESI) Requires: 291.1161 Found: 291.1158.

Additionally, the reaction could be carried out under higher concentration (0.028 M) using 1-(2-methylene-cyclopropyl)-but-3-en-1-one-tosyl-hydrazone (0.0460 g, 0.159 mmol), TMEDA (24.0 μ L, 0.160 mmol) and $MgCl_2$ (1.5 mg, 10 mol%) in DME (5.7 mL) at 120 °C for 5 hours. The title compound could be obtained after flash chromatography on silica using 7:3 dichloromethane:hexanes (R_f = 0.14) in 84% combined yield (0.0369 g of dienamine) and with a selectivity of > 20:1 over the azadiene product.

3-[3-(*tert*-Butyl-dimethyl-silanyloxy)-propyl]-5-methyl-1-(toluene-4-sulfonyl)-1,2-dihydro-pyridazine

According to the general procedure outlined above using 4-(*tert*-butyl-dimethyl-silanyloxy)-1-(2-methylene-cyclopropyl)-butan-1-one-tosyl-hydrazone (0.0200 g, 0.0473 mmol), TMEDA (7.0 μ L, 0.0467 mmol) and $MgCl_2$ (0.5 mg, 10 mol%) in DME (3.8 mL) at 120 °C for 4 hours, the title compound could be obtained after flash chromatography on silica using 3:7 hexanes:dichloromethane (R_f = 0.17) in 81% combined yield (0.0154 g of dienamine) and with a selectivity of > 20:1 over the azadiene product. Colorless oil. IR (neat, cm^{-1}) 3741, 3645, 2921, 2853, 1701, 1650, 1534, 1164, 1093; δ_H (400 MHz, $CDCl_3$) 8.42 (s, 1H), 7.56 (d, 2H, J = 8.2 Hz), 7.27 (d, 2H, J = 8.4 Hz), 6.25 (s, 1H), 5.60 (s, 1H), 3.45 (t, 2H, J = 5.86 Hz), 2.44 (s, 3H), 2.08 (t, 2H, J = 6.89 Hz), 1.97 (s, 3H), 1.26 (m, 2H), 0.91 (s, 9H), 0.11 (s, 6H); δ_C (100 MHz, $CDCl_3$) 149.8, 139.8, 134.9, 133.5, 123.3, 112.0, 110.0, 97.2, 67.2, 38.0, 31.2, 26.9, 25.2, 23.8, 17.2, 0.00; $C_{21}H_{35}N_2O_3SSi$ (MH^+) (ESI) Requires: 423.2132 Found: 423.2138.

3-[1,3]Dithian-2-yl-5-methyl-1-(toluene-4-sulfonyl)-1,2-dihydro-pyridazine

According to the general procedure outlined above using [1,3]-dithian-2-yl-(2-methylene-cyclopropyl)-methanone-tosyl-hydrazone (0.0148 g, 0.0402 mmol), TMEDA (6.0 μ L, 0.0400 mmol) and $MgCl_2$ (0.4 mg, 10 mol%) in DME (3.2 mL) at 120 °C for 4 hours, the title compound could be obtained after flash chromatography on silica using 1:1 dichloromethane:hexanes followed by 1:9 diethyl ether:toluene (R_f = 0.24) in 68% combined yield (0.0084 g of dienamine) and with a selectivity of 5:1 over the azadiene product.

For the major dienamine product: colorless oil. IR (neat, cm^{-1} , cm^{-1}) 3741, 3611, 3229, 2922, 2860, 1698, 1361, 1337, 1164, 1089; δ_{H} (400 MHz, CD_3CN) 8.56 (s, 1H), 7.66 (d, 2H, $J = 8.22$ Hz), 7.42 (d, 2H, $J = 8.22$ Hz), 5.95 (d, 1H, $J = 4.11$ Hz), 4.89 (s, 1H), 2.88 (td, 2H, $J = 12.13$, 2.15 Hz), 2.76 (dt, 2H, $J = 14.48$, 3.72 Hz), 2.45 (s, 3H), 2.04 (m, 2H), 1.88 (s, 3H), 1.70 (m, 3H); δ_{C} (100 MHz, CD_3CN) 147.0, 135.9, 132.3, 131.5, 129.5, 120.7, 119.2, 109.9, 41.4, 32.9, 26.4, 22.1, 12.2; $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}_2\text{S}_3$ (MH^+) (ESI) Requires: 369.0759 Found: 369.0763.

For the minor azadiene product: colorless oil, ($R_f = 0.3$ in 1:9 diethyl ether:toluene). IR (neat, cm^{-1}) 3604, 2922, 2853, 1693, 1647, 1354, 1167, 1086, 902; δ_{H} (400 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3$) 7.77 (d, 2H, $J = 8.36$ Hz), 7.42 (d, 2H, $J = 8.06$ Hz), 5.84 (m, 1H), 4.76 (s, 1H), 3.75 (s, 1H), 2.89 (m, 4H), 2.43 (s, 3H), 2.06 (m, 2H), 1.86 (s, 3H), 1.80 (m, 3H); δ_{C} (100 MHz, CD_3CN) 153.1, 146.4, 144.4, 133.3, 131.0, 130.1, 114.7, 49.7, 47.0, 30.5, 26.5, 22.0, 21.3; $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}_2\text{S}_3$ (MH^+) (ESI) Requires: 369.0759 Found: 369.0762.

5-Methyl-3-phenyl-1-(toluene-4-sulfonyl)-1,2-dihydro-pyridazine

According to the general procedure outlined above using (2-methylene-cyclopropyl)-phenyl-methanone-tosyl-hydrazone (0.0150 g, 0.0460 mmol), TMEDA (7.4 μL , 0.0494 mmol) and MgCl_2 (0.4 mg, 10 mol%) in DME (4.6 mL) at 120 $^\circ\text{C}$ for 4 hours, the title compound could be obtained after flash chromatography on silica using 1:1 dichloromethane:hexanes in 93% combined yield (0.0117 g of dienamine) and with a selectivity of 5:1 over the azadiene product.

For the major dienamine product: colorless oil, ($R_f = 0.11$). IR (neat, cm^{-1}) 3249, 2921, 2860, 1340, 1164; δ_{H} (400 MHz, CD_3CN) 8.64 (s, 1H), 7.38 (d, 2H, $J = 8.20$ Hz), 7.18-7.30 (m, 5H), 7.16 (d, 2H, $J = 8.20\text{Hz}$), 6.19 (s, 1H), 6.00 (d, 1H, $J = 1.95$ Hz), 2.37 (s, 3H), 1.96 (s, 3H); δ_{C} (100 MHz, CDCl_3) 144.9, 133.8, 133.1, 131.1, 129.6, 128.4, 128.1, 127.8, 126.7, 121.6, 118.2, 110.0, 21.8, 12.2; $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$ (MH^+) (ESI) Requires: 327.1161 Found: 327.1168.

For the minor azadiene product: colorless oil, ($R_f = 0.20$). IR (neat, cm^{-1}) 3611, 2915, 2853, 1698, 1514, 1446, 1337, 1157, 1086; δ_{H} (400 MHz, CD_3CN) 7.83 (d, 2H, $J = 8.20$ Hz), 7.70 (m, 2H), 7.43 (m, 5H), 6.36 (s, 1H), 3.81 (s, 2H), 2.41 (s, 3H), 1.97 (s, 3H); δ_{C} (100 MHz, CD_3CN) 151.0, 145.2, 143.0, 135.2, 132.4, 130.1, 130.0, 129.0, 128.9, 126.0, 113.3, 45.8, 20.9, 20.5; $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$ (MH^+) (ESI) Requires: 327.1161 Found: 327.1173.

Additionally, the reaction could be carried out under higher concentration (0.028 M) using (2-methylene-cyclopropyl)-phenyl-methanone-tosyl-hydrazone (0.0496 g, 0.152 mmol), TMEDA (22.8 μL , 0.152 mmol) and MgCl_2 (1.5 mg, 10 mol%) in DME (5.4 mL) at 120 $^\circ\text{C}$ for 5 hours, the title compound could be obtained after flash chromatography on silica using 1:1 dichloromethane:hexanes in 91% combined yield (0.0378 g of dienamine) and with a selectivity of 5:1 over the azadiene product.

3-Furan-2-yl-5-methyl-1-(toluene-4-sulfonyl)-1,2-dihydro-pyridazine

According to the general procedure outlined above using furan-2-yl-(2-methylene-cyclopropyl)-methanone-tosyl-hydrazone (0.0160 g, 0.0507 mmol), TMEDA (7.6 μ L, 0.0507 mmol) and MgCl_2 (0.5 mg, 10 mol%) in DME (4.1 mL) at 120 $^\circ\text{C}$ for 4 hours, the title compound could be obtained after flash chromatography on silica using 1:3 ethyl acetate:hexanes in 81% combined yield (0.0122 g of dienamine) and with a selectivity of 15:1 over the azadiene product. Colorless oil. (R_f = 0.3). IR (neat, cm^{-1}) 3611, 2922, 2846, 1715, 1354, 1164, 1086, 998; δ_{H} (400 MHz, CDCl_3) 7.81 (s, 1H), 7.36 (d, 2H, J = 8.36 Hz), 7.19 (m, 1H), 7.08 (d, 2H, J = 8.06 Hz), 6.58 (m, 1H), 6.18 (dd, 1H, J = 3.37, 1.91 Hz), 6.02 (d, 1H, J = 1.90 Hz), 5.90 (d, 1H, J = 2.93 Hz), 2.35 (s, 3H), 2.04 (s, 3H); δ_{C} (100 MHz, CDCl_3) 146.1, 144.9, 140.8, 133.0, 129.7, 128.2, 123.4, 121.4, 118.1, 111.3, 109.1, 105.4, 21.8, 12.1; $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$ (MH^+) (ESI) Requires: 317.0954 Found: 317.0951.

3,5-Dimethyl-2H-[1,2]oxazine and 3,5-Dimethyl-6H-[1,2]oxazine

According to the general procedure outlined above using 1-(2-methylene-cyclopropyl)-ethanone oxime (0.0329 g, 0.296 mmol), TMEDA (45.0 μ L, 0.300 mmol) and MgCl_2 (2.8 mg, 10 mol%) in DME (5.9 mL) at 120 $^\circ\text{C}$ for 18 hours, the title compound could be obtained after flash chromatography on silica using 1:4 diethyl ether:hexanes (R_f = 0.31) in 73% combined yield (0.0240 g) as a inseparable 3:1 mixture of the two regioisomers (major being the 2H-isomer) and as a clear colourless oil. IR (neat, cm^{-1}) 3142, 2923, 1621, 1537, 1441, 1383, 1334, 1204, 1139, 1035, 907, 784, 767, 704; δ_{H} (400 MHz, CDCl_3) 9.20 (bs, 0.75H), 6.37 (s, 0.75H), 5.98 (s, 0.25H), 5.49 (s, 0.75H), 3.87 (s, 0.50H), 2.13 (s, 2.25H), 2.07 (s, 0.75H), 1.99 (s, 2.25H), 1.96 (s, 0.75); δ_{C} (100 MHz, CDCl_3) 153.6, 145.4, 125.4, 123.4, 113.9, 113.1, 102.8, 68.8, 14.5, 12.2, 11.7, 10.4; $\text{C}_6\text{H}_{10}\text{NO}$ (MH^+) (ESI) Requires: 112.0756 Found: 112.0749.

General Procedure for the Azadiene

To an oven-dried flask, was added the MCP hydrazone (1 equiv), MgI_2 (1 equiv) and *N*-(benzylidene)-toluenesulfonamide (1.2 equiv). THF (0.02 M) was then added and the solution was stirred vigorously for 25 minutes at room temperature. The resulting white suspension was then heated to reflux (oil bath temperature = 86 °C) until judged complete by TLC. The resulting solution was cooled and quenched by the addition of a saturated sodium sulfite solution. The reaction solution was stirred for 20 minutes, extracted with ethyl acetate (3×50 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was then purified by chromatography on silica to afford the title compound.

3,5-Dimethyl-1-(toluene-4-sulfonyl)-1,6-dihydro-pyridazine

According to the general procedure outlined above using 1-(2-methylene-cyclopropyl)-ethanone-tosyl-hydrazone (0.0270 g, 0.101 mmol), *N*-(benzylidene)-toluenesulfonamide (0.0318 g, 0.123 mmol), MgI_2 (0.0285 g, 0.102 mmol) in THF (5.1 mL) for 15 hours, the title compound could be obtained after flash chromatography on silica using 1:2 ethyl acetate:hexanes (R_f = 0.4) in 86% yield (0.0232 g) and with a selectivity of > 20:1 over the dienamine product. Clear crystals, mp = 138-140 °C (CH_2Cl_2). IR (neat, cm^{-1}) 2914, 2809, 1662, 1595, 1493, 1441, 1223, 1121, 1090, 1033, 1010, 946, 901, 881, 814, 706, 665; δ_{H} (400 MHz, CDCl_3) 7.80 (d, 2H, J = 8.4 Hz), 7.33 (d, 2H, J = 7.9 Hz), 5.59 (s, 1H), 3.58 (s, 2H), 2.43 (s, 3H), 1.94 (s, 3H), 1.85 (s, 3H); δ_{C} (125 MHz, CDCl_3) 151.8, 144.2, 140.8, 132.4, 129.6, 129.0, 116.6, 45.5, 21.8, 21.7, 20.8; $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ (M^+) (EI) Requires: 264.0933 Found: 264.0930.

5-Methyl-3-phenyl-1-(toluene-4-sulfonyl)-1,6-dihydro-pyridazine

According to the general procedure outlined above using (2-methylene-cyclopropyl)-phenyl-methanone-tosyl-hydrazone (0.0417 g, 0.128 mmol), *N*-(benzylidene)-toluenesulfonamide (0.0390 g, 0.150 mmol), MgI_2 (0.0350 g, 0.126 mmol) in THF (6.4 mL) for 3 hours, the title compound could be obtained after flash chromatography on silica using 1:3 THF:hexanes (R_f = 0.31) in 72% yield (0.0300 g) and with a selectivity of > 20:1 over the dienamine product.

Mechanistic Studies

3,3-Dideuterio-2-methylene-cyclopropanecarboxylic acid

This compound was prepared using Lautens' procedure for the samarium-mediated cyclopropanation of allenic alcohols.⁵ To a slurry of samarium metal (14.5 g, 96.4 mmol) in THF (387 mL) at room temperature, was added HgCl₂ (2.62 g, 9.65 mmol). The reaction was stirred for 30 minutes at room temperature, after which a solution of buta-2,3-dien-1-ol (1.23 g, 17.5 mmol) in THF (252 mL) was added. The resulting slurry was stirred for an additional 25 minutes at room temperature before being cooled to -78 °C. CD₂I₂ (26.2 g, 97.1 mmol) was then added dropwise over the period of several hours. The resulting blue solution was allowed to warm slowly to room temperature and was stirred overnight before being quenched with a saturated aqueous K₂CO₃ solution. The slurry was then extracted with ether (3×75 mL) and the combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated *in vacuo*. The crude mixture was passed through a short plug of silica to remove any remaining metals using 1:1 diethyl ether:pentane to afford the 3,3-dideuterio-2-methylenecyclopropyl alcohol (approximately 0.878 g, 58% NMR yield) which was used in the next step without further purification.

To a solution of the 3,3-dideuterio-2-methylenecyclopropyl alcohol (0.878 g, 10.2 mmol) in acetone (17.3 mL) at -10 °C, was slowly added a solution of CrO₃ (4.00 g, 40.0 mmol) in concentrated sulfuric acid (4.2 mL) and water (12 mL) until the reaction was judged complete. The reaction was then quenched with saturated sodium sulfite and dichloromethane (50 mL) and water (30 mL) were added. The resulting organic layer was removed, and the aqueous layer was washed with dichloromethane (3×75 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated *in vacuo*. The crude mixture was then purified by flash chromatography on silica using 1:1 diethyl ether:pentane (*R_f* = 0.48) followed by additional purification via an acid/base extraction to afford the title compound in 43% yield over two steps (74% yield on the oxidation) (0.758 g). δ_{H} (400 MHz, CDCl₃) 5.57 (s, 2H), 2.26 (s, 1H); δ_{D} (46 MHz, CHCl₃) 1.86 (bs, 1D), 1.69 (bs, 1D).

3,3-Dideuterio-2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide

The title compound was prepared in 93% yield (0.200 g, 1.40 mmol) according to the procedure outlined on page SI-3 using 3,3-dideuterio-2-methylene-cyclopropanecarboxylic acid (0.150 g, 1.50 mmol). δ_{H} (400 MHz, CDCl₃) 5.52 (d, 1H, *J* = 2.5 Hz), 5.46 (s, 1H), 3.78 (s, 3H), 3.23 (s, 3H), 2.80 (bs, 1H); δ_{D} (46 MHz, CHCl₃) 1.86 (bs, 1D), 1.59 (bs, 1D).

1-(3,3-Dideuterio-2-methylene-cyclopropyl)-ethanone-tosyl-hydrazone

The title compound was prepared as a 2.3:1 mixture in 68% yield over two steps (0.254 g, 0.954 mmol) according to the procedure outlined on page SI-4 using 3,3-dideuterio-2-methylene-cyclopropanecarboxylic acid methoxy-methyl-amide (0.200 g, 1.40 mmol). δ_{H} (400 MHz, CDCl_3) 7.37 (d, 1.4H, $J = 8.2$ Hz), 7.36 (d, 0.7H, $J = 8.2$ Hz), 7.57 (bs, 0.3H), 7.33 (d, 2H, $J = 8.0$ Hz), 7.14 (bs, 0.7H), 5.54 (d, 0.3H, $J = 2.3$ Hz), 5.52 (d, 0.7H, $J = 2.3$ Hz), 5.49 (d, 0.3H, $J = 1.8$ Hz), 5.46 (d, 0.7H, $J = 1.6$ Hz), 2.44 (s, 3H), 2.39 (bs, 0.7H), 2.25 (bs, 0.3H), 1.71 (s, 0.9H), 1.49 (s, 2.1H); δ_{D} (46 MHz, CHCl_3) 1.31 (bs, 2D).

5-dideuteriomethyl-3-methyl-1-(toluene-4-sulfonyl)-1,2-dihydro-pyridazine

The title compound was prepared in 77% yield (0.0154 g, 0.0578 mmol) according to the procedure outlined on page SI-9 using 1-(3,3-dideuterio-2-methylene-cyclopropyl)-ethanone-tosyl-hydrazone (0.0199 g, 0.0747 mmol). δ_{H} (400 MHz, CDCl_3) 7.67 (d, 2H, $J = 8.2$ Hz), 7.31 (d, 2H, $J = 8.0$ Hz), 6.99 (bs, 1H), 5.98 (s, 1H), 5.60 (s, 1H), 2.46 (s, 3H), 1.92 (s, 1H), 1.87 (s, 3H); δ_{D} (46 MHz, CHCl_3) 1.91 (bs, 2D).

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- ⁴ Although this change in E/Z isomer ratio upon crystallization was unexpected, such observations in other hydrazone and imine systems have been reported, see: a) Raban, M.; Carlson, E. *J. Am. Chem. Soc.* **1971**, *93*, 685. b) Bellamy, A. J.; Guthrie, R. D. *J. Chem. Soc. C.* **1968**, 2090. c) Curtin, D. Y.; Hausser, J. W. *J. Org. Chem.* **1961**, *83*, 3474.
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