Supporting Information

Design, Synthesis, and Reactivity of 1-Hydrazinodienes For Use in Organic Synthesis

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General: Scandium(III) triflate and tris(dibenzylideneacetone)dipalladium chloroform adduct were purchased from Strem Chemical. Unless otherwise stated, all reagents were purchased from Aldrich and used without further purification. Methylene chloride, tetrahydrofuran, toluene, and pyridine were dried by passing through activated alumina columns. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plated (60 F₂₅₄) using UV light as a visualizing agent and aqueous potassium permanganate and heat as a developing agent. E. Merck silica gel 60 (230-400 mesh) was used for flash column chromatography.

Instrumentation: FT-IR spectra were obtained on a Perkin-Elmer Paragon 500. Nuclear magnetic resonance (NMR) spectra were taken on a Varian Inova-500, Inova-400, and Mercury-Vx-300 instruments. Proton chemical shifts are reported in parts per million and are calibrated to the residual protium (7.24 ppm) in the CDCl₃ NMR solvent. Carbon chemical shifts are reported in parts per million and are calibrated to the solvent peaks (77 ppm). Coupling constant values were extracted assuming first-order coupling. The multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad signal. High resolution mass spectra were obtained using an Agilent ESI-TOF mass spectrometer.

***t*-Butyl-allyloxycarbazate (S2):**¹ *t*-Butyl carbazate **S1** (13.2 g, 100 mmol), pyridine (8.9 mL, 110 mmol), and diethyl ether (400 mL) were combined in a 1000 mL round-bottom flask under argon. The reaction mixture was then cooled to 0 °C and allylchloroformate (10.61 mL, 100 mmol) was added dropwise over 5 min. The mixture was then stirred at 0 °C for 45 min whereupon the reaction was warmed to ambient temperature and stirred for an additional 45 min. The organics were then washed with H₂O (1x75 mL), 5% HCl (1x75 mL), and 5% NaHCO₃ (1x75 mL). The combined organics were dried with Na₂SO₄ and the solvent was removed by rotary evaporation to provide *t*-butyl-allyloxycarbazate (**S2**) as a white solid (19.8 g, 92%). ¹H NMR (400 MHz, CDCl₃) δ 6.55 (s, 1H), 6.35 (s, 1H), 5.88 (m, 1H), 5.31 (d, 1H, J = 17.2 Hz), 5.21 (d, 1H, J = 10.4 Hz), 4.61 (dd, 2H, J = 1.2 Hz, J = 5.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 156.54, 155.66, 131.97, 118.29, 81.72, 66.49, 28.09; IR (thin film, cm⁻¹) 3306, 2981, 1714, 1506, 1245, 1162. HRMS (EI) C₉H₁₆N₂O₄ ([M]⁺) 216.1110, found 216.1114.

Allyloxycarbazate (S3): *t*-Butyl-allyloxyformyl carbazate **S2** (30.85 g, 143 mmol) and H₂O (200 mL) were added to a 500 mL round-bottom flask equipped with a reflux condenser. The reaction flask was placed in an oil bath and heated to 160 °C for 2 hours. The mixture was allowed to cool to ambient temperature and then extracted with diethyl ether (5x50 mL). The combined organics were dried with Na₂SO₄ and the solvent was removed by rotary evaporation to provide allyloxycarbazate (**S3**) as a clear oil (13.6 g, 82%). ¹H NMR (400 MHz, CDCl₃) δ 6.61 (s, 1H), 5.83 (m, 1H), 5.22 (d, 1H, J = 17.2 Hz), 5.14 (d, 1H, J = 10.0 Hz), 4.52 (d, 2H, J = 4.0 Hz), 3.77 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 158.26, 132.14, 117.67, 65.72; IR (thin film, cm⁻¹) 3340, 1716, 1647, 1506, 1277, 1182, 1064. HRMS (EI) C₄H₈N₂O₂ ([M]⁺) 116.0586, found 116.0590.

¹ Gordon, M. S.; Krause, J. G.; Linneman-Mohr, M. A.; Parchue, R. R. *Synthesis*, **1980**, 3, 244–245.

(3-Methyl-but-2-enylidene)-carbamic acid allyl ester (6**):** Allyloxycarbamate **S3** (7.6, 65.1 mmol), 3-methyl-2-butenal (6.9 mL, 71.6 mmol), and THF (260 mL) were added to a 1000 mL round-bottom flask and the reaction mixture was stirred for 16 h. The solvent was removed by rotary evaporation and excess 3-methyl-2-butenal was removed in *vacuo* to provide 3-methyl-but-2-enylidene)-carbamic acid allyl ester **6** as a clear oil (11.1 g, 94%). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.72 (s, 1H), 6.05 (d, 1H, J = 9.2 Hz), 5.93 (m, 1H), 5.32 (d, 1H, J = 16.8 Hz), 5.22 (dd, 1H, J = 1.2 Hz, J = 10.4 Hz), 4.69 (m, 2H), 1.85 (d, 3H, J = 2.4 Hz), 1.82 (d, 3H, J = 2.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 153.66, 144.47, 132.03, 121.63, 117.57, 104.72, 65.53, 26.00, 18.25; IR (thin film, cm⁻¹) 3224, 3049, 2973, 2912, 1721, 1648, 1543, 1376, 1248, 1032; HRMS (EI) C₉H₁₄N₂O₂ ([M]⁺) 182.1055, found 182.1054.

(3-Methyl-but-2-enylidene)-biscarbamic acid allyl ester (S4**):** (3-Methyl-but-2-enylidene)-carbamic acid allyl ester (**6**) (11.1 g, 70 mmol) and THF (350 mL) were added to a flame dried 1 L round-bottom flask under argon. The mixture was cooled to -78 °C and LHMDS in (1 M solution in hexanes, 70 mmol) was added dropwise over 5 min. The reaction was then stirred for an additional 30 min at -78 °C. Allylchloroformate (7.85 mL, 74 mmol) was added in one portion and the reaction mixture was allowed to warm to ambient temperature and stirred for an additional 1.5 h. The reaction mixture was concentrated by half by rotary evaporation and diethyl ether (50 mL) was added. The mixture was then washed with saturated NaHCO₃ (2x50 mL). The organics were dried with Na₂SO₄ and the solvent was removed by rotary evaporation to provide a yellow oil. The residue was purified by flash chromatography (2:1 hexanes/ethyl acetate) to afford pure bisAlloc hydrazone **S4** (12.2 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, 1H, J = 10.0 Hz), 6.19 (d, 1H, J = 10.0 Hz), 5.93 (m, 2H), 5.36 (d, 2H, J = 16.8 Hz), 5.25 (d, 2H, J = 10.4 Hz), 4.73 (d, 4H, J = 5.6 Hz), 1.93 (s, 3H), 1.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.85, 152.12, 151.59, 131.29, 121.44, 118.99, 67.82, 26.85, 19.13; IR (thin film, cm⁻¹) 1790, 1752, 1262, 1108; HRMS (EI) C₁₃H₁₈N₂O₄ ([M]⁺) 266.1267, found 266.1261.

1-Hydrazinodiene (7**):** (3-Methyl-but-2-enylidene)-biscarbamic acid allyl ester **S4** (1 g, 3.75 mmol) and pyridine (1.5 mL, 18.75 mmol) were added to a flame-dried 10 mL round-bottom flask. Methanesulfonic chloride (0.87 mL, 11.25 mmol) was added dropwise over 1 min and the reaction was sealed and stirred at ambient temperature for 2 h. The mixture was purified by flash chromatography (3:1 hexanes/ethyl acetate) to provide pure 1-hydrazinodiene **7** (1.04 g, 80%). ¹H NMR (400 MHz, CDCl₃) δ 6.63 (d, 1H, J = 14.0 Hz), 5.91 (m, 2H), 5.61 (d, 1H, J = 14.0 Hz), 5.40 (d, 2H, J = 16.4 Hz), 5.28 (d, 2H, J = 9.8 Hz), 4.86 (d, 2H, J = 3.4 Hz), 4.76 (m, 4H), 3.16 (s, 3H), 1.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.14, 138.79, 130.46, 123.74, 119.5, 115.65, 114.00, 68.88, 41.50, 18.83; IR (thin film, cm⁻¹) 1807, 1775, 1364, 1244, 1166, 1112; HRMS (ESI) C₁₄H₂₀N₂O₆Na ([M+Na]⁺) 367.0934, found 367.0926.

Synthesis of Diels–Alder adduct **8**

General procedure for the scandium(III) triflate (10 mol%) catalyzed Diels–Alder reaction: Scandium(III) triflate (24.6 mg, 0.05 mmol) and 4Å-molecular sieves (75 mg) were added to a 15 mL recovery flask and the system was first flame dried under vacuum and then allowed to cool to ambient temperature under argon. 1-Hydrazinodiene **7** (172.5 mg, 0.5 mmol) and methylene chloride (2.5 mL) were added the flask and the mixture was stirred for 2 min. The unsaturated aldehyde (1.5 mmol) was then added and the reaction was sealed with a yellow Teflon cap. The reaction was stirred for the specified length of time at 23 °C. The reaction mixture was then filtered through florisil, and the solvent was removed by rotary evaporation to provide a yellow oil. The residue was purified by flash chromatography to provide pure product **8**.

Methacrolein Diels–Alder adduct 8a: Reaction time: 3 hours. The product was isolated as a 5:1 mixture of inseparable isomers (185 mg, 89%). The relative stereochemistry of the major diastereomer was determined by nOe studies of derivative **9a** (see p S-5). ¹H NMR (500 MHz, CDCl₃) δ 9.96 (s, 1H), 5.89 (m, 2H), 5.36 – 5.42 (m, 3H), 5.24 – 5.30 (m, 2H), 4.65 – 4.75 (m, 3H), 4.53 – 4.57 (m, 1H), 4.45 (d, 1H, J = 4.5 Hz), 3.26 (s, 3H), 1.94 – 2.07 (m, 2H), 1.69 – 1.92 (m, 2H), 1.66 (s, 3H), 1.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 204.96, 154.79, 152.74, 142.04, 130.81, 130.57, 119.81, 119.65, 115.20, 69.08, 68.48, 61.43, 47.11, 41.68, 26.14, 24.51, 23.42, 20.00; IR (thin film, cm⁻¹) 2939, 1799, 1766, 1722, 1448, 1350, 1324, 1302, 1242, 1207, 1158, 1109, 992, 962, 937; HRMS (ESI) C₁₈H₂₆N₂O₇SNa ([M+Na]⁺) 437.1353, found 437.1357.

Crotonaldehyde Diels–Alder adduct 8b: Reaction time: 3 hours. The major isomer was isolated as a clear oil (135 mg, 65%). The relative stereochemistry of the major diastereomer was determined by analogy with adduct **8d**. ¹H NMR analysis of the crude reaction mixture reveals the aldehyde corresponding to the major exo-diastereomer is upfield from the endo-diastereomer. ¹H NMR (400 MHz, CDCl₃) δ 9.85 (d, 1H, J = 2 Hz), 5.88 – 5.98 (m, 2H), 5.51 (s, 1H), 5.39 – 5.44 (m, 2H), 5.28 – 5.31 (m, 2H), 5.01 (d, 1H, J = 10.0 Hz), 4.62 – 4.79 (m, 4H), 3.08 (s, 3H), 2.46 – 2.52 (m, 1H), 1.80 – 1.91 (m, 3H), 1.63 (s, 3H), 1.04 (d, 3H, J = 6.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 204.21, 153.47, 153.26, 139.07, 130.60, 119.84, 119.57, 68.97, 68.82, 58.17, 54.38, 41.81, 38.28, 32.67, 22.99, 18.98; IR (thin film, cm⁻¹) 2963, 2934, 1802, 1771, 1742, 1446, 1352, 1326, 1241, 1158, 1110, 966; HRMS (ESI) C₁₈H₂₆N₂O₇SNa ([M+Na]⁺) 437.1353, found 437.1345.

2-Hexenal Diels–Alder adduct 8c: Reaction time: 12 hours. The major isomer was isolated as a clear oil (100 mg, 45%). The relative stereochemistry of the major diastereomer was determined by analogy with adduct **8d**. ¹H NMR analysis of the crude reaction mixture reveals the aldehyde corresponding to the major exo-diastereomer is upfield from the endo-diastereomer. ¹H NMR (500 MHz, CDCl₃) δ 0.85 (t, 3H, J = 7 Hz), 1.24–1.14 (m, 1H), 1.32–1.24 (m, 1H), 1.48–1.34 (m, 2H), 1.63 (s, 3H), 1.78–1.70 (m, 1H), 1.90–1.81 (m, 1H), 1.98–1.92 (m, 1H), 2.60–2.55 (m, 1H), 3.06 (s, 3H), 4.80–4.60 (m, 4H), 5.10–4.95 (m, 1H), 5.31–5.27 (m, 2H), 5.46–5.39 (m, 2H), 5.51 (s, 1H), 5.98–5.88 (m, 2H), 9.86 (d, 1H, J = 2.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 14.05, 19.31, 23.15, 34.77, 35.11, 37.59, 41.81, 52.95, 58.46, 68.85, 69.00, 119.55, 119.61, 119.87, 130.63, 138.92, 153.27, 153.53, 184.54, 189.65, 204.61; IR (thin film, cm⁻¹) 2959, 2933, 1801, 1770, 1352, 1240, 1158, 1100; HRMS (ESI) C₂₀H₃₀N₂O₇SNa (M+Na)⁺ 465.1666, found 465.1656 m/z.

Cinnamaldehyde Diels–Alder adduct 8d: Reaction time: 3 hours. The major isomer was isolated as a white solid (173 mg, 72%). The relative stereochemistry of the major diastereomer was determined by x-ray crystallographic analysis. See p S-15 for crystal structure data. ¹H NMR (500 MHz, CDCl₃) δ 9.30 (s, 1H), 7.31 (t, 2H, J = 7.5 Hz), 7.19 – 7.25 (m, 3H), 5.94 (m, 2H), 5.65 (s, 1H), 5.39 – 5.48 (m, 2H), 5.28 – 5.32 (m, 2H), 5.16 (d, 1H, J = 8.0 Hz), 4.66 – 4.79 (m, 4H), 3.17 (dt, 1H, J = 1.5 Hz, J = 6.0 Hz), 3.06 (s, 3H), 2.87 (dt, 1H, J = 4.5 Hz, J = 12.0 Hz), 2.33 (t, 1H, J = 15.0 Hz), 2.04 (dd, 1H, J = 4.5 Hz, J = 17.5 Hz), 1.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 203.34, 153.70, 153.01, 140.32, 138.74, 130.65, 130.57, 124.02, 127.49, 120.24, 120.16, 119.69, 69.10, 68.90, 58.10, 52.68, 44.81, 41.99; IR (thin film, cm⁻¹) 2914, 1801, 1769, 1739, 1453, 1352, 1327, 1240, 1156, 1109, 1032, 966; HRMS (ESI) C₂₃H₂₈N₂O₇SNa (M+Na)⁺ 499.1509, found 499.1497 m/z.

Acrolein Diels–Alder adduct 8e: Reaction time: 3 hours. The major isomer was isolated as a clear oil (94 mg, 47%). The relative stereochemistry of the major diastereomer was determined by analogy with adduct **8d**. ¹H NMR analysis of the crude reaction mixture reveals the aldehyde corresponding to the major exo-diastereomer is upfield from the endo-diastereomer. ¹H NMR (500 MHz, CDCl₃) δ 9.67 (s, 1H), 5.86 – 5.94 (m, 2H), 5.45 (s, 1H), 5.38 – 5.43 (m, 2H), 5.28 (d, 2H, J = 10.0 Hz), 4.95 (s, 1H), 4.64 – 4.72 (m, 4H), 3.16 (s, 3H), 2.81 – 2.85 (m, 1H), 1.93 – 2.01 (m, 2H), 1.83 – 1.87 (m, 1H), 1.66 – 1.70 (m, 1H), 1.64 (s, 3H); ¹³C

NMR (125 MHz, CDCl₃) δ 201.65, 153.48, 153.34, 141.25, 130.59, 130.56, 119.92, 119.68, 118.20, 68.93, 68.87, 56.01, 48.63, 41.91, 27.24, 23.47, 21.59; IR (thin film, cm⁻¹) 3021, 2936, 1802, 1769, 1740, 1449, 1351, 1328, 1242, 1215, 1155, 1108; HRMS (ESI) C₁₇H₂₄N₂O₇SNa (M+Na)⁺ 423.1196, found 423.1177 *m/z*.

Methyl vinyl ketone Diels-Alder adduct 8f: Reaction time: 3 hours. The major isomer was isolated as a clear oil (136 mg, 66%). The relative stereochemistry of the major diastereomer was determined by coupling constants of derivative **9f** (see p S-6). ¹H NMR (500 MHz, CDCl₃) δ 5.87 – 5.93 (m, 2H), 5.49 (s, 1H), 5.37 – 5.42 (m, 2H), 5.26 – 5.27 (m, 2H), 4.90 (d, 1H, *J* = 8 Hz), 4.62 – 4.74 (m, 3H), 4.58 – 4.60 (m, 1H), 3.08 (s, 3H), 2.79 – 2.84 (m, 1H), 2.14 (s, 3H), 1.92 – 2.04 (m, 2H), 1.80 – 1.84 (m, 1H), 1.61 (s, 3H), 1.46 – 1.54 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 208.63, 153.80, 153.01, 139.30, 130.61, 119.88, 119.52, 119.41, 68.87, 68.68, 57.21, 49.50, 41.73, 28.53, 28.28, 25.50, 23.21; IR (thin film, cm⁻¹) 3020, 2936, 1800, 1769, 1743, 1713, 1650, 1449, 1350, 1327, 1303, 1244, 1155, 1113, 1034, 965; HRMS (ESI) C₁₈H₂₆N₂O₇SNa (M+Na)⁺ 437.1353, found 437.1342 *m/z*.

General procedure for the scandium(III) triflate (30 mol%) catalyzed Diels-Alder reaction: Scandium(III) triflate (185 mg, 0.43 mmol) and 4Å-molecular sieves (215 mg) were added to a 15 mL recovery flask and the system was flame dried under vacuum and then allowed to cool to ambient temperature under argon. 1-Hydrazinodiene **7** (500 mg, 1.4 mmol) and methylene chloride (4 mL) were added the flask and the mixture was stirred for 2 min. The unsaturated ester (4.3 mmol) was then added and the reaction was sealed with a yellow Teflon cap. The reaction was stirred for the specified length of time at 23 °C. The reaction mixture was then filtered through florisil, and the solvent was removed by rotary evaporation to provide a yellow oil. The residue was purified by flash chromatography to provide pure product **8**.

Diethyl maleate Diels-Alder adduct 8g: Reaction time: 15 hours. The product was purified by flash chromatography (3:1 hexanes/ethyl acetate) to provide **8g** as a clear oil (567 mg, 76%). The relative stereochemistry of the major diastereomer was determined by nOe studies of **13a**. ¹H NMR (500 MHz, CDCl₃) δ 1.18 (t, 3H, *J* = 7 Hz), 1.23 (t, 3H, *J* = 7 Hz), 1.68 (s, 3H), 2.19 (dd, 1H, *J* = 6, 18.5 Hz), 2.33 (dd, 1H, *J* = 10, 18.5 Hz), 3.08 (ddd, 1H, *J* = 4, 6, 10 Hz), 3.19 (s, 3H), 3.70-3.67 (m, 1H), 4.10-4.05 (m, 2H), 4.16-4.11 (m, 2H), 4.77-4.64 (m, 4H), 4.98 (s, 1H), 5.29-5.24 (m, 2H), 5.35-5.33, 1H), 5.43-5.36 (m, 2H), 5.96-5.85 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 13.93, 14.12, 23.56, 28.83, 37.16, 42.68, 44.36, 57.67, 60.70, 61.07, 68.83, 68.86, 115.71, 119.63, 119.71, 130.60, 141.95, 153.06, 170.37, 172.76; IR (thin film, cm⁻¹) 2983, 2939, 1804, 1770, 1732, 1447, 1354, 1242, 1108, 1033; HRMS (ESI) C₂₂H₃₂N₂O₁₀SNa (M+Na)⁺ 539.167, found 539.1674 *m/z*.

Diethyl fumarate Diels-Alder adduct 8h: Reaction time: 16 hours. The product was purified by flash chromatography (3:1 hexanes/ethyl acetate) to provide **8h** as a clear oil (225 mg, 30%). The relative stereochemistry of the major diastereomer was determined by nOe studies of **13b**. ¹H NMR (500 MHz, CDCl₃) δ 1.21 (t, 6H, *J* = 7 Hz), 1.63 (s, 3H), 2.02 (dd, 1H, *J* = 4.5, 17 Hz), 2.36-2.38 (m, 1H), 2.84-2.73 (m, 2H), 3.13 (s, 3H), 4.14-3.99 (m, 4H), 4.76-4.59 (m, 4H), 5.03-4.99 (m, 1H), 5.26 (d, 2H, *J* = 9.5 Hz), 5.38-5.35 (m, 1H), 5.42-5.39 (m, 1H), 5.59 (s, broad, 1H), 5.95-5.85 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 13.88, 13.98, 22.86, 31.62, 41.75, 44.39, 44.86, 60.58, 60.92, 61.24, 68.75, 68.86, 119.41, 119.48, 120.21, 130.69, 136.69, 153.18, 153.48, 172.26, 172.61; IR (thin film, cm⁻¹) 2984, 2939, 1802, 1770, 1738, 1446, 1353, 1240, 1157, 1113, 1033; HRMS (ESI) C₂₂H₃₂N₂O₁₀SNa (M+Na)⁺ 539.1670, found 539.1676 *m/z*.

General procedure for the diethylaluminum chloride catalyzed Diels–Alder reaction: 1-Hydrazinodiene **7** (172.5 mg, 0.5 mmol) and toluene (2.5 mL) were added to a flame dried, 15 mL recovery flask under argon. The unsaturated aldehyde was added followed by diethyl aluminum chloride (1.8 M solution in toluene, 56 μ L, 0.1 mmol). The reaction was sealed with a yellow Teflon cap and stirred for the specified length of time at 23 °C. The reaction mixture was then filtered through florisil, and the solvent was removed by rotary evaporation to provide a yellow oil. The residue was purified by flash chromatography to provide pure product **8**.

Methacrolein Diels–Alder adduct 8a: Reaction time: 2.5 hours. The product was isolated as a 12:1 mixture of inseparable isomers (169 mg, 81%). The relative stereochemistry of the major diastereomer was determined by nOe studies of derivative **9a** (see p S-5). ¹H NMR (500 MHz, CDCl₃) δ 9.96 (s, 1H), 5.89 (m, 2H), 5.36 – 5.42 (m, 3H), 5.24 – 5.30 (m, 2H), 4.65 – 4.75 (m, 3H), 4.53 – 4.57 (m, 1H), 4.45 (d, 1H, J = 4.5 Hz), 3.26 (s, 3H), 1.94 – 2.07 (m, 2H), 1.69 – 1.92 (m, 2H), 1.66 (s, 3H), 1.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 204.96, 154.79, 152.74, 142.04, 130.81, 130.57, 119.81, 119.65, 115.20, 69.08, 68.48, 61.43, 47.11, 41.68, 26.14, 24.51, 23.42, 20.00; IR (thin film, cm⁻¹) 2939, 1799, 1766, 1722, 1448, 1350, 1324, 1302, 1242, 1207, 1158, 1109, 992, 962, 937; HRMS (ESI) C₁₈H₂₆N₂O₇S ([M+Na]⁺) 437.1353, found 437.1357.

Deprotection of Diels–Alder adduct **8**

1-Methanesulfonyl-3 α ,6-dimethyl-3 α ,4,5,7 α -tetrahydro-1H-indazole (9a**):** Diels–Alder adduct **8a** (150 mg, 0.36 mmol), acetic acid (98.9 μ L, 1.7 mmol), bistriphenylphosphinepalladium dichloride (10.1 mg, 0.014 mmol), and methylene chloride (7.2 mL) were added to a 25 mL round-bottom flask under argon. Tributyltin hydride (212.5 μ L, 0.79 mmol) was added in one portion and the reaction was stirred for 1 h. The product was purified by flash chromatography (first hexanes, then 1:1 hexanes/ethyl acetate) to provide a clear oil. The product was purified two more times by flash chromatography (1:1 hexanes/ethyl acetate) to provide 1-methanesulfonyl-3 α ,6-dimethyl-3 α ,4,5,7 α -tetrahydro-1H-indazole as a clear oil (56 mg, 68%). ¹H NMR (500 MHz, CDCl₃) δ 6.92 (s, 1H), 5.72 (s, 1H), 3.91 (m, 1H), 3.06 (s, 3H), 1.98 – 2.03 (m, 2H), 1.78 (s, 3H), 1.68 – 1.76 (m, 1H), 1.60 – 1.66 (m, 1H), 1.23 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 157.50, 139.92, 116.88, 64.50, 48.49, 37.21, 28.22, 26.14, 23.74, 20.94; IR (thin film, cm⁻¹) 2967, 2932, 1672, 1602, 1447, 1348, 1163, 1071, 982; HRMS (ESI) C₁₀H₁₆N₂O₂S ([M+Na]⁺) 251.0830, found 251.0811.

The following selected nOe was observed for heterocycle **9a**:

This nOe can only be observed with a *cis*-fused ring system (A). If the rings were *trans*-fused (B), the methyl group and the methyne proton would both be pseudoaxial and no nOe would be observed.

1-Methanesulfonyl-3,6-dimethyl-3 α ,4,5,7 α -tetrahydro-1H-indazole (9f): Diels–Alder adduct **8f** (33 mg, 0.08 mmol), acetic acid (22.0 μ L, 0.38 mmol), bistrisphenylphosphinepalladium dichloride (2.3 mg, 0.0032 mmol), and methylene chloride (1.6 mL) were added to a 25 mL round-bottom flask under argon. Tributyltin hydride (47.2 μ L, 0.18 mmol) was added in one portion and the reaction was stirred for 1 h. The product was purified by flash chromatography (first hexanes, then 1:1 hexanes/ethyl acetate) to provide a white solid. The product was purified again by flash chromatography (1:1 hexanes/ethyl acetate) to provide 1-methanesulfonyl-3,6-dimethyl-3 α ,4,5,7 α -tetrahydro-1H-indazole as a white solid (10 mg, 55%). ^1H NMR (500 MHz, CDCl_3) δ 1.59–1.62 (m, 1H), 1.67 (s, 3H), 2.04 (s, 3H), 2.11–2.19 (m, 3H), 2.65 (t, 1H, J = 14 Hz), 2.97 (s, 3H), 3.67 (d, 1H, J = 14 Hz), 6.09 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.44, 21.89, 22.70, 31.17, 34.81, 51.87, 66.34, 120.72, 137.71, 163.31; IR (thin film, cm^{-1}) 853.9, 961.9, 1054.8, 1076.9, 1163.2, 1342.7, 1433.0, 2916.3.

If the rings were *cis*-fused (A), there would be a small coupling constant between H_a and H_b . However, the large observed coupling constant (J = 14 Hz) is consistent with the vicinal, axial relationship of H_a and H_b in the *trans*-fused rings (B).

General procedure for the acetal protection of Diels–Alder adduct 8: Diels–Alder adduct **8**, *p*-toluenesulfonic acid (5 mol%), and 1:5 toluene/ethylene glycol (0.25 M) were added to a 10 mL round-bottom flask equipped with a reflux condenser. The reaction was then heated to 80 $^\circ\text{C}$ for 2 h. The reaction mixture was then poured into saturated NaHCO_3 (10 mL) and extracted with methylene chloride (3x20 mL). The combined organics were dried with Na_2SO_4 and the solvent was removed by rotary evaporation to provide a clear oil. The residue was purified by flash chromatography (3:1 hexanes/ethyl acetate) to provide pure acetal **10**.

Acetal 10a: The reaction was run with 0.34 mmol **8a**. The product was isolated as a clear oil (146 mg, 79%). ^1H NMR (500 MHz, CDCl_3) δ 5.84 – 5.94 (m, 2H), 5.35 – 5.43 (m, 3H), 5.24 – 5.28 (m, 3H), 4.61 – 4.73 (m, 4H), 4.21 (d, 1H, J = 6 Hz), 3.87 – 3.94 (m, 2H), 3.78 – 3.85 (m, 2H), 3.25 (s, 3H), 1.89 – 2.03 (m, 2H), 1.65 (s, 3H), 1.49 – 1.53 (m, 1H), 0.82 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.88, 153.54, 139.96, 130.86, 130.68, 119.29, 119.14, 117.53, 105.75, 68.71, 68.53, 65.67, 64.85,

61.50, 42.12, 40.16, 26.00, 24.30; IR (thin film, cm^{-1}) 2945, 2886, 1764, 1745, 1448, 1346, 1319, 1240, 1193, 1145, 1100, 977, 932; HRMS (ESI) $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_8\text{Sna}$ ($[\text{M}+\text{Na}]^+$) 481.1615, found 481.1623.

Acetal 10b: The reaction was run with 0.27 mmol **8b**. The product was isolated as a clear oil (90.8 mg, 75%). ^1H NMR (500 MHz, CDCl_3) δ 5.21 (s, 1H), 4.92 (d, 1H, $J = 3.0$ Hz), 4.70 (d, 1H, $J = 14$ Hz), 3.82 – 3.99 (m, 4H), 3.32 (s, 2H), 3.00 (s, 3H), 1.88 – 2.02 (m, 4H), 1.71 (s, 3H), 1.52 – 1.58 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.33, 119.65, 104.32, 65.38, 65.02, 56.69, 39.01, 37.84, 29.35, 23.39, 21.42; IR (thin film, cm^{-1}) 3368, 2928, 2896, 1307, 1152, 1035, 957. HRMS (ESI) $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_8\text{Sna}$ ($[\text{M}+\text{Na}]^+$) 481.1615, found 481.1607 m/z .

Acetal 10c: The reaction was run with 0.3 mmol **8c**. The product was isolated as a clear oil (145 mg, 98%). ^1H NMR (300 MHz, CDCl_3) δ 0.82 (t, 3H, $J = 7$ Hz), 1.24–1.08 (m, 2H), 1.44–1.28 (m, 2H), 1.63 (s, 3H), 1.82–1.66 (m, 2H), 1.98–1.88 (m, 1H), 2.16–2.08 (m, 1H), 3.22 (s, 3H), 3.85–3.75 (m, 2H), 4.00–3.90 (m, 2H), 4.80–4.54 (m, 5H), 5.01 (d, 1H, $J = 2$ Hz), 5.28–5.21 (m, 2H), 5.37 (s, 1H), 5.44–5.40 (m, 2H), 5.98–5.82 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.22, 19.85, 23.82, 32.57, 33.60, 36.24, 41.81, 42.86, 58.02, 64.46, 64.67, 68.58, 68.64, 104.82, 118.37, 119.23, 130.67, 130.83, 140.97, 153.45, 153.73; IR (thin film, cm^{-1}) 2958, 2932, 1800, 1767, 1349, 1240, 1157; HRMS (ESI) $\text{C}_{22}\text{H}_{34}\text{N}_2\text{O}_8\text{Sna}$ ($[\text{M}+\text{Na}]^+$) 509.1928, found 509.1930 m/z .

Acetal 10d: The reaction was run with 0.29 mmol **8d**. The product was isolated as a clear oil (127 mg, 88%). ^1H NMR (500 MHz, CDCl_3) δ 7.26 – 7.28 (m, 2H), 7.17 – 7.22 (m, 3H), 5.98 (m, 2H), 5.27 (s, 1H), 5.43 – 5.50 (m, 2H), 5.29 – 5.34 (m, 2H), 5.05 (s, 1H), 4.71 – 4.85 (m, 4H), 3.85 (m, 1H), 3.73 (m, 1H), 3.57 (m, 1H), 3.28 (s, 3H), 3.17 (m, 1H), 2.99 (m, 1H), 2.70 (m, 1H), 2.29 (t, 1H, $J = 13.0$ Hz), 1.98 (m, 1H), 1.74 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.98, 153.54, 144.31, 142.30, 130.95, 130.74, 128.04, 127.98, 126.07, 119.42, 119.01, 103.55, 68.83, 68.76, 65.04, 64.14, 59.64, 43.75, 42.48, 42.16, 37.86, 23.37; IR (thin film, cm^{-1}) 3028, 2891, 1798, 1766, 1352, 1323, 1301, 1240, 1205, 1157, 1116, 1030, 961; HRMS (ESI) $\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}_8\text{Sna}$ ($[\text{M}+\text{Na}]^+$) 543.1771, found 543.1768 m/z .

Acetal 10e: The reaction was run with 0.27 mmol **8e**. The product was isolated as a clear oil (109.1 mg, 93%). ^1H NMR (500 MHz, CDCl_3) δ 5.86 – 5.96 (m, 2H), 5.36 – 5.44 (m, 2H), 5.35 (s, 1H), 5.25 – 5.28 (m, 1H), 5.07 (d, 2H, $J = 4.0$ Hz), 4.64 – 4.77 (m, 4H), 4.58 (m, 1H), 3.81 – 3.97 (m, 4H), 3.20 (s, 3H), 2.12 – 2.17 (m, 1H), 1.86 – 1.90 (m, 2H), 1.70 – 1.77 (m, 1H), 1.64 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.90, 153.45, 142.31, 130.78, 130.72, 119.57, 119.50, 117.77, 103.28, 68.81, 68.77, 65.20, 65.06, 58.04, 41.53, 39.47, 27.33, 23.67; IR (thin film, cm^{-1}) 2935, 1801, 1767, 1450, 1350, 1326, 1303, 1242, 1212, 1158, 1121, 1034, 962; HRMS (ESI) $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}_8\text{Sna}$ ($[\text{M}+\text{Na}]^+$) 467.1458, found 467.1451 m/z .

Acetal 10f: The reaction was run with 0.28 mmol **8f**. The product was isolated as a clear oil (100 mg, 76%). ^1H NMR (500 MHz, CDCl_3) δ 5.87 – 5.96 (m, 2H), 5.45 (s, 1H), 5.39 – 5.42 (m, 2H), 5.26 – 5.28 (m, 2H), 4.51 – 4.74 (m, 4H), 4.51 (s, 1H), 3.86 – 3.92 (m, 4H), 3.71 (s, 3H), 2.52 (m, 1H), 1.92 – 1.95 (m, 1H), 1.75 – 1.85 (m, 2H), 1.64 (s, 3H), 1.51 – 1.57 (m, 1H), 1.23 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.77, 152.98, 141.52, 130.81, 130.73, 119.52, 119.19, 117.45, 111.20, 68.70, 68.49, 65.01, 63.87, 54.96, 43.20, 41.63, 25.94, 23.91; IR (thin film, cm^{-1}) 2938, 2891, 1800, 1767, 1447, 1348, 1326, 1245, 1214, 1159, 1104, 1039, 949; HRMS (ESI) $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_8\text{Sna}$ ($[\text{M}+\text{Na}]^+$) 481.1615, found 481.1606 m/z .

General procedure for Alloc deprotections:² Acetal protected, Diels–Alder adduct **10** (1 equiv) and THF (0.2 M) were added to a flame dried, 10 mL round bottom flask under argon. Diethyl amine (15 equiv) was added via syringe, followed by tris(dibenzylideneacetone)dipalladium chloroform adduct ($\text{Pd}_2(\text{dba})_3$) (5 mol%) and 1,2-bis(diphenylphosphino)ethane (dppe)

² Genêt, J. P.; Blart, E.; Savignac, M.; Lemeune, S.; Lemaire-Audoire, S.; Bernard, J. M. *Synlett*. **1993**, 680–682.

(10 mol%), the reaction flask was capped with a yellow Teflon cap, and the mixture was stirred for 30 min. The solvent was removed by rotary evaporation and the residue was purified by flash column chromatography to provide deprotected hydrazine **11**.

Deprotected hydrazine 11a: The reaction was run with 0.20 mmol **10a**. The product was isolated as a white solid (35 mg, 60%). ^1H NMR (400 MHz, CDCl_3) δ 5.16 (d, 1H, $J = 2.8$ Hz), 4.80 (s, 1H), 4.37 (s, 1H), 3.92 (m, 2H), 3.86 (m, 1H), 3.82 (m, 1H), 2.99 (s, 3H), 1.99 (m, 2H), 1.85 (m, 1H), 1.75 (s, 3H), 1.45 (m, 1H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.05, 116.24, 107.19, 65.35, 64.83, 58.13, 39.25, 37.65, 26.32, 25.52, 23.58, 20.12; IR (thin film, cm^{-1}) 2935, 2360, 1319, 1143, 1096;

HRMS (ESI) $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_4\text{Sna}$ ($[\text{M}+\text{Na}]^+$) 313.1192, found 313.1188.

Deprotected hydrazine 11b: The reaction was run with 0.16 mmol **10b**. The product was isolated as a white solid (41 mg, 90%). ^1H NMR (500 MHz, CDCl_3) δ 5.16 (s, 1H), 5.08 (s, 1H), 4.80 (d, 1H, $J = 9.0$ Hz), 3.97 – 4.02 (m, 2H), 3.81 – 4.01 (m, 2H), 3.53 (s, 2H), 2.98 (s, 3H), 1.87 – 1.95 (m, 2H), 1.71 – 1.79 (m, 2H), 1.69 (s, 3H), 1.03 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 142.62, 119.33, 103.63, 64.93, 64.72, 55.98, 43.20, 39.46, 37.90, 29.85, 23.19, 19.89; IR (thin film, cm^{-1}) 3360, 2892, 1309, 1156, 1126, 1033, 962, 918, 783; HRMS (ESI) $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_4\text{Sna}$ ($[\text{M}+\text{Na}]^+$) 313.1192, found 313.1184.

Deprotected hydrazine 11c: The reaction was run with 0.29 mmol **10c**. The product was isolated as a white solid (59 mg, 65%). ^1H NMR (500 MHz, CDCl_3) δ 0.86 (t, 3H, $J = 7$ Hz), 1.28–1.16 (m, 2H), 1.42–1.32 (m, 1H), 1.62–1.54 (m, 1H), 1.69 (s, 3H), 1.76–1.65 (m, 1H), 1.88–1.80 (m, 2H), 1.98–1.93 (m, 1H), 2.97 (s, 3H), 3.46 (s, br, 2H), 3.86–3.76 (m, 2H), 4.02–3.96 (m, 2H), 4.82–4.76 (m, 1H), 5.07 (s, 1H), 5.15 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.35, 19.05, 23.34, 34.16, 35.15, 35.44, 37.90,

41.35, 55.84, 64.81, 103.55, 119.17, 142.40; IR (thin film, cm^{-1}) 3360, 2958, 2912, 1620, 1439, 1311, 1155, 1037; HRMS (ESI) $\text{C}_{14}\text{H}_{27}\text{N}_2\text{O}_4\text{S}$ ($\text{M}+\text{H}^+$) 319.1686, found 319.1672 m/z .

Deprotected hydrazine 11d: The reaction was run with 0.22 mmol **10d**. The product was isolated as a white solid (70 mg, 94%). ^1H NMR (500 MHz, CDCl_3) δ 7.28 – 7.31 (m, 2H), 7.19 – 7.26 (m, 3H), 5.30 (s, 1H), 5.03 (s, 1H, $J = 9.0$ Hz), 4.63 (s, 1H), 3.85 – 3.88 (m, 1H), 3.62 – 3.67 (m, 4H), 3.52 (s, 2H), 3.01 (s, 3H), 2.42 – 2.46 (m, 1H), 2.25 – 2.31 (m, 1H), 2.10 (dd, 1H, $J = 17.5$ Hz, $J = 4.5$ Hz), 1.74 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.47, 141.92, 128.45, 127.78, 126.48, 119.94, 103.36,

64.83, 55.28, 42.30, 42.13, 39.30, 38.06, 23.07; IR (thin film, cm^{-1}) 3359, 3027, 2895, 1311, 1152, 1030, 954; HRMS (ESI) $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$ (M^+) 353.1529, found 153.1529 m/z .

Deprotected hydrazine 11e: The reaction was run with 0.11 mmol **10e**. The product was isolated as a white solid (20 mg, 65%). ^1H NMR (500 MHz, CDCl_3) δ 5.21 (s, 1H), 4.92 (d, 1H, $J = 3.0$ Hz), 4.70 (d, 1H, $J = 14$ Hz), 3.82 – 3.99 (m, 4H), 3.32 (s, 2H), 3.00 (s, 3H), 1.88 – 2.02 (m, 4H), 1.71 (s, 3H), 1.52 – 1.58 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.33, 119.65, 104.32, 65.38, 65.02, 56.69, 39.01, 37.84, 29.35, 23.39, 21.42; IR (thin film, cm^{-1}) 3368, 2928, 2896, 1307, 1152, 1035, 957;

HRMS (ESI) $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_4\text{Sna}$ ($\text{M}+\text{Na}^+$) 299.1036, found 299.1030 m/z .

Deprotected hydrazine 11f: The reaction was run with 0.22 mmol **10a**. The product was isolated as a white solid (52 mg, 82%). ^1H NMR (500 MHz, CDCl_3) δ 5.19 (s, 1H), 4.71 (d, 1H, $J = 9.0$ Hz), 3.96 (m, 1H), 3.88 (m, 3H), 3.57 (s, 2H), 2.99 (s, 3H), 1.90 – 2.08 (m, 3H), 1.82 (m, 1H), 1.66 (s, 3H), 1.45

(m, 1H), 1.26 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.25, 121.21, 110.94, 64.90, 63.75, 56.61, 43.97, 38.21, 30.04, 24.02, 22.97, 19.83; IR (thin film, cm^{-1}) 3361, 2967, 2934, 2891, 1445, 1379, 1308, 1199, 1153, 1050, 958; HRMS (ESI) $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_4\text{Sna} (\text{M}+\text{Na})^+$ 313.1192, found 313.1185 m/z .

Deprotected hydrazine 11g: The reaction was run with 0.50 mmol **8g**. The product was isolated as a white solid (95 mg, 54%). ^1H NMR (500 MHz, CDCl_3) δ 121-1.16 (m, 6H), 1.71 (s, 3H), 2.37-2.25 (m, 2H), 2.99 (s, 3H), 3.13 (dd, 1H, $J = 4.5, 6.5$ Hz), 3.37-3.34 (m, 1H), 3.58 (s, br, 2H), 4.16-4.02 (m, 4H), 4.96-4.92 (m, 1H), 5.26 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.98, 23.46, 30.25, 37.82, 39.94, 43.79, 54.74, 60.71, 60.80, 118.06, 140.38, 171.50, 172.67; IR (thin film, cm^{-1}) 3367, 2981, 2936, 2360, 2341, 1733, 1320, 1197, 1151; HRMS (ESI) $\text{C}_{14}\text{H}_{25}\text{N}_2\text{O}_6\text{S} (\text{M}+\text{H})^+$ 349.1428, found 349.1416 m/z .

Deprotected hydrazine 11h: The reaction was run with 0.38 mmol **8f**. The product was isolated as a white solid (38 mg, 28%). ^1H NMR (300 MHz, CDCl_3) δ 1.25-1.20 (m, 6H), 1.72 (s, 3H), 2.20-2.07 (m, 1H), 2.32 (dd, 1H, $J = 5.4, 17$ Hz), 2.86 (dd, 1H, $J = 11, 12$ Hz), 2.96 (s, 3H), 3.06 (ddd, 1H, $J = 5.4, 12, 12$ Hz), 3.67 (s, 2H), 4.22-4.09 (m, 4H), 4.88-4.80 (m, 1H), 5.31 (s, br, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.08, 14.16, 22.84, 32.49, 38.18, 41.73, 44.74, 58.23, 60.97, 61.02, 120.04, 140.04, 172.61, 173.15; IR (thin film, cm^{-1}) 3369, 2981, 2936, 1732, 1335, 1188, 1155; HRMS (ESI) $\text{C}_{14}\text{H}_{24}\text{N}_2\text{O}_6\text{Sna} (\text{M}+\text{Na})^+$ 371.1247, found 371.1233 m/z .

General procedure for the elimination/rearrangement of deprotected hydrazine (11): Deprotected hydrazine **11** (1 equiv), tetrabutylammonium acetate (4 equiv), and THF (0.2 mmol) were added to a 15 mL round-bottom flask equipped with a reflux condenser. The reaction was stirred for 18 h at 40 °C. The mixture was then allowed to cool to ambient temperature and diluted with 10% diethyl ether/pentane. The organics were washed with 2 mL H_2O and the combined organics were dried with Na_2SO_4 and removed by rotary evaporation. The product was purified by flash column chromatography (1:9 diethyl ether/pentanes) to provide pure cyclohexene **12**.

Cyclohexene 12a: The reaction was run with 0.07 mmol **11a**. The product was isolated as a clear oil (11.2 mg, 86%). ^1H NMR (500 MHz, CDCl_3) δ 5.57 (dd, 1H, $J = 2.3$ Hz, $J = 10.0$ Hz), 5.46 (d, 2H, $J = 10.5$ Hz), 4.56 (s, 1H), 3.93 (m, 2H), 3.84 (m, 2H), 2.12 (m, 1H), 1.73 (m, 1H), 1.63 (dt, 1H, $J = 3.5$ Hz, $J = 13.0$ Hz), 1.44 (m, 1H), 1.20 (m, 1H), 0.98 (s, 3H), 0.95 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 134.37, 130.51, 109.52, 65.31, 65.26, 39.02, 30.61, 29.69, 29.50, 27.60, 21.64; IR (thin film, cm^{-1}) 2947, 2924, 2850, 2358, 2336, 1456, 1098.

Cyclohexene 12b: The reaction was run with 0.14 mmol **11b**. The product was isolated as a clear oil (23 mg, 92%). ^1H NMR (500 MHz, CDCl_3) δ 5.70 (d, 1H, $J = 10.0$ Hz), 5.55 (d, 1H, $J = 10.0$ Hz), 4.78 (d, 1H, $J = 4.5$ Hz), 3.94 (m, 2H), 3.82 (m, 2H), 2.19 (m, 1H), 1.94 (m, 2H), 1.46 (m, 1H), 1.36 (m, 1H), 0.96 - 1.02 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.15, 123.53, 106.01, 65.01, 64.79, 45.61, 35.97, 26.99, 26.15, 21.29, 20.07; IR (thin film, cm^{-1}) 3024, 2956, 2926, 2873, 1458, 1405, 1376, 1146, 1123, 1057, 1037, 966.

Cyclohexene 12c: The reaction was run with 0.14 mmol **11c**. The product was isolated as a clear oil (26 mg, 87%). ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, 3H, $J = 6.5$ Hz), 0.95 (d, 3H, $J = 7$ Hz), 1.37-1.25 (m, 5H), 1.55-1.49 (m, 1H), 1.87-1.82 (m, 1H), 2.02-1.98 (m, 1H), 2.17-2.09 (m, 1H), 3.85-3.81 (m, 2H), 4.00-3.90 (m, 2H), 4.75 (d, 1H, $J = 5.5$ Hz), 5.57-5.53 (m, 1H), 5.71-5.66 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.24, 20.25, 21.38, 26.27, 31.61, 32.61, 35.53, 43.78, 64.68, 65.03, 106.36, 123.71, 123.78, 135.52, 135.58; IR (thin film, cm^{-1}) 2955, 2926, 2871, 1453, 1123, 1053.

Cyclohexene 12d: The reaction was run with 0.17 mmol **11d**. The product was isolated as a clear oil (31 mg, 81%). ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.18 (m, 5H), 5.88 – 5.83 (m, 1H), 5.80 – 5.76 (m, 1H), 4.68 (d, 1H, $J = 4.0$ Hz), 3.98 – 3.89 (m, 2H), 3.82 – 3.75 (m, 2H), 2.98 (ddd, 1H, $J = 3.5$ Hz, $J = 8.0$ Hz, $J = 11.0$ Hz), 2.69 – 2.63 (m, 1H), 2.21 (s, 1H), 1.96 – 1.88 (m, 1H), 1.64 – 1.57 (m, 1H), 1.05 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 145.55, 135.36, 128.32, 127.58, 126.06, 123.92, 104.69, 65.23, 64.92, 44.31, 37.89, 37.29, 28.35, 21.05; IR (thin film, cm^{-1}) 3026, 2956, 2923, 2872, 1603, 1494, 1453, 1404, 1366, 1149, 1134, 1053, 1038, 945, 756, 701.

Cyclohexene 12e: The reaction was run with 0.08 mmol **11e**. The product was isolated as a clear oil (9 mg, 94%). ^1H NMR (500 MHz, CDCl_3) δ 5.72 (d, 1H, $J = 10.0$ Hz), 5.61 (d, 1H, $J = 10.0$ Hz), 4.68 (d, 1H, $J = 6.0$ Hz), 3.91 – 3.99 (m, 2H), 3.84 (m, 2H), 2.26 (m, 1H), 2.16 (m, 1H), 1.67 (m, 3H), 1.38 (m, 1H), 0.97 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 135.94, 124.83, 106.70, 65.04, 64.83, 39.15, 29.52, 28.19, 21.24; IR (thin film, cm^{-1}) 3023, 2955, 2927, 2870, 1454, 1393, 1148, 1118, 1082.

Cyclohexene 12f: The reaction was run with 0.15 mmol **11f**. The product was isolated as a clear oil (25 mg, 91%). ^1H NMR (500 MHz, CDCl_3) δ 5.70 (m, 1H), 5.62 (d, 1H, $J = 10.0$ Hz), 3.93 (m, 4H), 2.29 (m, 1H), 2.15 (m, 1H), 1.66 (m, 2H), 1.57 (m, 1H), 1.45 (m, 1H), 1.24 (s, 3H), 0.97 (d, 3H, $J = 7.5$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 135.06, 126.03, 111.71, 64.66, 64.62, 43.76, 28.90, 28.58, 21.13, 21.05, 20.50; IR (thin film, cm^{-1}) 3022, 2955, 2871, 1456, 1378, 1210, 1150, 1048, 947.

Elimination/rearrangement to form cyclohexene 13

Cyclohexene 13a: Deprotected hydrazine **11g** (38 mg, 0.109 mmol) was dissolved in MeOH (0.7 mL) and sodium acetate (13 mg, 0.163 mmol) was added. The reaction was monitored by TLC and stirred for 24 h at ambient temperature. After 24 h TLC indicated the absence of starting material and the MeOH was removed in vacuo. The residue was purified by column chromatography (9:1 hexanes/ethyl acetate) to yield 24 mg (91%) of **13a** as a clear oil. ^1H NMR (500 MHz, CDCl_3) δ 1.01 (d, 3H, $J = 6.5$ Hz), 1.23-1.19 (m, 6H), 1.68-1.59 (m, 1H), 2.24-2.17 (m, 2H), 2.59 (ddd, 1H, $J = 2.5, 5.5, 12.5$ Hz), 3.51-3.47 (m, 1H), 4.25-4.03 (m, 4H), 5.73-5.65 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.11, 21.04, 29.44, 31.09, 41.24, 42.15, 60.42, 60.59, 122.23, 136.54, 172.04, 173.42; IR (thin film, cm^{-1}) 2960, 2873, 1741, 1263, 1191; HRMS (ESI) $\text{C}_{13}\text{H}_{20}\text{O}_4\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 263.1254, found 263.1255 m/z .

The following selected nOe was observed for cyclohexene **13a**:

The observed nOe between H_a and H_b is consistent with structure **A** as H_a and H_b are both pseudoaxial and in close proximity. However, no nOe would be observed between H_a and H_b for diastereomer **B**.

Cyclohexene 13b: Deprotected hydrazine **11h** (25 mg, 0.07 mmol) was dissolved in MeOH (0.46 mL) and sodium acetate (8.8 mg, 0.105 mmol) was added. The reaction was monitored by TLC and stirred for 24 h at ambient temperature. After 24 h TLC indicated the absence of starting material and the MeOH was removed in vacuo. The residue was purified by column chromatography (9:1 hexanes/ethyl acetate) to yield 8 mg (48%) of **13b** as a clear oil. ^1H NMR (500 MHz, CDCl_3) δ 1.02 (d, 3H, $J = 7$ Hz), 1.24 (t, 6H, $J = 7$ Hz), 1.68 (ddd, app dt, 1H, $J = 4, 4, 13$ Hz), 1.91 (ddd, 1H, $J = 6, 10.5, 13.5$ Hz), 2.31–2.24 (m, 1H), 3.00 (ddd, 1H, $J = 3.5, 8, 11$ Hz), 3.49–3.45 (m, 1H), 4.14 (q, 4H, $J = 7.5$ Hz), 5.73–5.66 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.13, 14.19, 20.56, 28.04, 31.19, 38.11, 43.38, 60.65, 60.90, 122.19, 134.38, 173.01, 174.87; IR (thin film, cm^{-1}) 2960, 2873, 1733, 1195, 1161.

The following selected nOe was observed for cyclohexene **13b**:

The observed nOe between methyne proton H_a and the methyl group is consistent with structure **A** as both substituents are pseudoaxial and are in close proximity. This nOe is not consistent with diastereomer **B** as the two groups are on opposite sides of the ring.

Synthesis of *trans*-fused decalin **16**

Mono-Alloc hydrazone (S5): Allyloxycarbamate **S3** (3.91, 33.7 mmol), aldehyde³ (5 g, 40 mmol), and THF (200 mL) were added to a 500 mL round-bottom flask and the reaction mixture was stirred for 3 h. The solvent was removed by rotary evaporation and the residual oil was purified by column chromatography to yield 5.2 g (71%) of **S-5** as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 1.52–1.62 (m, 6H), 2.16–2.21 (m, 2H), 2.26–2.32 (m, 2H), 4.68 (s, br, 2H), 5.22 (dd, 1H, J = 1, 10 Hz), 5.32 (d, 1H, J = 16 Hz), 5.93 (s, br, 1H), 6.00 (d, 1H, J = 10 Hz), 7.79 (s, br, 1H), 7.91 (s, br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 26.19, 27.60, 28.14, 19.38, 37.27, 65.66, 66.27, 117.82, 118.62, 132.15, 143.85, 151.83, 153.40; IR (thin film, cm⁻¹) 3229, 2931, 2854, 1718, 1648, 1543, 1247; HRMS (ESI) C₁₂H₁₉N₂O₂ (M+H)⁺ 223.1441, found 223.1448 *m/z*.

Bis-Alloc Hydrazone S6: Mono Alloc hydrazone **S5** (1.0 g, 4.5 mmol) and THF (22 mL) were added to a flame dried 250 mL round-bottom flask under argon. The mixture was cooled to –78 °C and LHMDS (1 M solution in hexanes, 4.5 mL, 4.5 mmol) was added dropwise over 5 min. The reaction was then stirred for an additional 30 min at –78 °C. Allylchloroformate (0.5 mL, 4.72 mmol) was added via syringe and the reaction mixture was allowed to warm to ambient temperature and stirred for an additional 1.5 h. The reaction mixture was diluted with diethyl ether (50 mL) and then washed with saturated NaHCO₃ (2x20 mL). The organics were dried with Na₂SO₄ and the solvent was removed by rotary evaporation to provide a yellow oil. The residue was purified by flash chromatography (2:1 hexanes/ethyl acetate) to afford pure bisAlloc hydrazone **S6** as a clear oil (1.3 g, 94). ¹H NMR (500 MHz, CDCl₃) δ 1.54–64 (m, 6H), 2.20–2.25 (m, 2H), 2.30–2.34 (m, 2H), 4.68–4.72 (m, 4H), 5.19–5.23 (m, 2H), 5.33 (dd, 2H, J = 1.5, 16.5 Hz), 5.86–5.94 (m, 2H), 6.10 (d, 1H, J = 10 Hz), 8.22 (dd, 1H, J = 1.2, 10 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 26.13, 27.74, 28.13, 29.89, 37.75, 67.66, 118.14, 118.82, 131.16, 151.45, 159.83, 164.12; IR (thin film, cm⁻¹) 2934, 2857, 1790, 1750, 1646, 1262, 1109; HRMS (ESI) C₁₆H₂₃N₂O₄ (M+H)⁺ 307.1652, found 307.1648 *m/z*.

Synthesis of 14: Bis-Alloc hydrazone **S6** (570 mg, 1.86 mmol) and pyridine (0.75 mL, 9.3 mmol) were added to a flame-dried 10 mL round-bottom flask. Methanesulfonyl chloride (0.43 mL, 5.5 mmol) was added dropwise over 1 min and the reaction was sealed and stirred at ambient temperature for 2 h. The reaction was diluted with methylene chloride and washed with 10% NH₄Cl (1x10 mL), 10% NaHCO₃ (1x10 mL), and H₂O (1x10 mL). The combined organics were dried with Na₂SO₄ and the solvent was removed by rotary evaporation to provide an orange oil. The residue was purified by flash chromatography (85:15 hexanes/ethyl acetate) to provide pure **14** as a clear oil (1.04 g, 78%). ¹H NMR (500 MHz, CDCl₃) δ 1.59–1.52 (m, 2H), 1.69–1.62 (m, 2H), 2.11–2.05 (m, 4H), 3.14 (s, 3H), 4.81–4.72 (m, 4H), 5.28 (dd, 2H, J = 1, 10 Hz), 5.41 (dd, 2H, J = 1.5, 17), 5.56 (d, 1H, J = 14 Hz), 5.63 (s, 1H), 5.96–5.87 (m, 2H), 6.52 (d, 1H, J = 14); ¹³C NMR (100 MHz, CDCl₃) δ 22.06, 22.14, 24.46, 25.58, 41.08, 68.58, 115.69, 119.14, 120.18, 128.43, 130.42, 132.25, 151.11; IR (thin film, cm⁻¹) 2943, 1806, 1775, 1645, 1365, 1245, 1164, 1110; HRMS (ESI) C₁₇H₂₅N₂O₆S (M+H)⁺ 385.1428, found 385.1412 *m/z*.

³ Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682.

Synthesis of 15: 4Å-Molecular sieves (150 mg/mmol) were added to a 25 mL round bottom flask and the system was flame dried under vacuum and charged with argon when cool. Toluene (2.2 mL) was added followed by 1-hydrazinodiene **14** (245 mg, 0.64 mmol) as a 1 mL solution in toluene. Diethylaluminum chloride (1.8 M solution in toluene, 0.14 mL, 0.25 mmol) was added to the reaction followed by methacrolein (0.16 mL, 1.9 mmol). The reaction was stirred under argon for 24 h at ambient temperature and then purified by column chromatography without aqueous work-up to provide 135 mg (50%) of clear oil **15** as a 7.3:1 mixture of diastereomers. The relative stereochemistry of the major diastereomer was determined by analogy with Diels–Alder adduct **8a**. ^1H NMR analysis of the crude reaction mixture reveals the aldehyde corresponding to the major endo-diastereomer is downfield from the exo-diastereomer. An analytical sample was obtained after 3 chromatography columns. ^1H NMR (500 MHz, CDCl_3) δ 0.98 (s, 3H), 1.22–1.08 (m, 2H), 1.40–1.28 (m, 2H), 1.89–1.68 (m, 4H), 2.02–1.90 (m, 2H), 2.26–2.19 (m, 1H), 3.26 (s, 3H), 4.43–4.40 (m, 1H), 4.54 (dddd, app ddt, $J = 1, 1, 6, 13$ Hz, 1H), 4.64 (dddd, app ddt, $J = 1, 1, 6, 13$ Hz, 1H), 4.76–4.70 (m, 2H), 5.30–5.24 (m, 3H), 5.39–5.35 (m, 1H), 5.45–5.40 (m, 1H), 5.96–5.85 (m, 2H), 9.94 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 20.61, 25.77, 27.11, 31.12, 33.74, 34.50, 34.82, 41.73, 47.76, 60.93, 68.41, 69.01, 112.29, 119.63, 119.81, 130.30, 130.81, 148.33, 152.70, 154.50, 205.10; IR (thin film, cm^{-1}) 2932, 2854, 1767, 1721, 1448, 1351, 1240, 1203, 1156; HRMS (ESI) $\text{C}_{21}\text{H}_{30}\text{N}_2\text{O}_7\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 477.1666, found 477.1665 m/z .

Synthesis of acetal S7: Diels–Alder adduct **15** (120 mg, 0.263 mmol), *p*-toluenesulfonic acid (5 mol%), and 1:5 toluene/ethylene glycol (0.25 M) were added to a 10 mL round-bottom flask equipped with a reflux condenser. The reaction was then heated to 80 °C for 2 h. The reaction mixture was then poured into saturated NaHCO_3 (10 mL) and extracted with methylene chloride (3x20 mL). The combined organics were dried with Na_2SO_4 and the solvent was removed by rotary evaporation to provide clear oil. The residue was purified by flash chromatography (3:1 hexanes/ethyl acetate) to provide pure acetal **S7** as a clear oil (120 mg, 92%). ^1H NMR (500 MHz, CDCl_3) δ 0.84 (s, 3H), 1.00–1.40 (m, 4H), 1.57–1.64 (m, 1H), 1.68–1.79 (m, 3H), 1.86–1.98 (m, 2H), 2.14–2.22 (m, 1H), 3.28 (s, 3H), 3.80–3.94 (m, 4H), 4.25–4.29 (m, 1H), 4.58–4.64 (m, 1H), 4.66–4.79 (m, 3H), 5.34–5.36 (m, 2H), 5.37–5.39 (m, 1H), 5.36–5.48 (m, 3H), 5.85–5.98 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 15.95, 26.11, 26.97, 32.59, 33.97, 34.25, 34.91, 41.16, 42.17, 62.05, 64.82, 65.09, 68.49, 68.70, 105.63, 114.90, 119.10, 119.46, 130.61, 130.83, 145.87, 153.32, 153.80; IR (thin film, cm^{-1}) 2931, 1768, 1749, 1635, 1347, 1320, 1238, 1196; HRMS (ESI) $\text{C}_{23}\text{H}_{34}\text{N}_2\text{O}_8\text{S}$ ($\text{M}+\text{Na}$) $^+$ 521.1928, found 521.1928 m/z .

Synthesis of 16: Acetal **S7** (120 mg, 0.24 mmol) and THF (1.2 mL) were added to a flame dried, 10 mL round bottom flask under argon. Diethyl amine (0.375 mL, 3.6 mmol) was added via syringe. The septa was removed and tris(dibenzylideneacetone)dipalladium chloroform adduct ($\text{Pd}_2(\text{dba})_3$) (12 mg, 0.012 mmol) and 1,2-bis(diphenylphosino)ethane (dppe) (10 mg, 0.24 mmol) were quickly added. The reaction was stirred 30 minutes at ambient temperature or until TLC indicated the absence of starting material at which point tetrabutylammonium acetate was added (288 mg, 0.96 mmol). The reaction was heated to 35 °C and stirred 18 h overnight. The reaction was diluted with a 1:1 mixture of pentane and diethyl ether and the organic layer washed with H_2O (2x) and sat. NaCl (1x), dried over Na_2SO_4 , and filtered. The solvent was removed in vacuo and the residual oil purified by column chromatography (95:5 pentane-ether) to yield 37 mg (70%) of **16** as a clear oil. ^1H NMR (500 MHz, CDCl_3) δ 1.00 (s, 3H), 0.94–1.08 (m, 2H), 1.13–1.24 (m, 1H),

1.25–1.33 (m, 3H), 1.36–1.43 (m, 1H), 1.54–1.62 (m, 2H), 1.66–1.76 (m, 3H), 3.80–3.89 (m, 2H), 3.90–3.96 (m, 2H), 4.53 (s, 1H), 5.39–5.42 (m, 1H), 5.50 (d, 1H, $J = 10$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 22.26, 26.70, 26.82, 32.72, 33.40, 36.89, 37.45, 40.93, 42.42, 65.22, 65.33, 109.64, 130.58, 133.27; IR (thin film, cm^{-1}) 2921, 2851, 1447, 1116; HRMS (ESI) $\text{C}_{14}\text{H}_{22}\text{O}_2$ ($\text{M}+\text{Na}$) $^{+}$ 245.1512, found 245.1504 m/z .

Crystal Structure Data for **8d**:

Single-Crystal X-ray Analysis of 8d: Single crystals for X-ray diffraction were obtained from diethyl ether. A colorless needle cut to 0.12 mm x 0.20 mm x 0.33 mm in size was mounted on a glass fiber with silicone grease and then transferred to a Nonius KappaCCD diffractometer equipped with an MSC X-stream cryosystem and MoK α radiation ($\lambda = 0.71073$ Angstroms). Eight hundred frames of data were collected at 200(2) K with an omega oscillation range of 1.0 deg/frame and an exposure time of 40 sec/°.(Nonius, 1998) A total of 18,122 reflections (thetamax = 27.56 deg) were indexed, integrated and corrected for Lorentz and polarization effects using DENZO-SMN and SCALEPACK.(Otwinowski & Minor, 1997) Data reduction yielded 5646 unique reflections ($R_{int} = 0.048$) of which 3986 had $I > 2\sigma(I)$. Post-refinement of the unit cell parameters gave $a = 9.9186(6)$ Å, $b = 11.3368(6)$ Å, $c = 11.9916(6)$ Å, $\alpha = 89.263(2)^\circ$, $\beta = 67.540(2)^\circ$, $\gamma = 80.873(2)^\circ$, and $V = 1228.66(12)$ Å³. Axial photographs and a lack of systematic absences were consistent with the compound having crystallized in the triclinic space group P1 or P-1. The latter centrosymmetric space group P-1 (No. 2) was selected based on an observed mean $|E^*E-1|$ value of 0.970 (versus the expectation values of 0.968 and 0.736 for centric and noncentric data, respectively).

Table S1: Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j.$$

	Occupancy	x	y	z	U_{eq}
C1	1	0.4456 (2)	0.5161 (2)	0.1899 (2)	0.0391 (5)
H1	1	0.4012	0.5462	0.1307	0.047
C2	1	0.5603 (3)	0.4086 (2)	0.1306 (2)	0.0446 (5)
H2	1	0.5269	0.3374	0.1191	0.054
C3	1	0.7055 (3)	0.4061 (2)	0.0929 (2)	0.0441 (5)
C4	1	0.7684 (3)	0.5165 (2)	0.1004 (2)	0.0435 (5)
H4A	1	0.8564	0.5197	0.0255	0.052
H4B	1	0.8011	0.5116	0.1689	0.052
C5	1	0.6568 (2)	0.6314 (2)	0.1175 (2)	0.0407 (5)
H5	1	0.6364	0.6402	0.0421	0.049
C6	1	0.5094 (2)	0.6184 (2)	0.2228 (2)	0.0390 (5)
H6	1	0.5293	0.5994	0.2973	0.047
C7	1	0.8153 (3)	0.2939 (2)	0.0410 (3)	0.0596 (7)
H7A	1	0.7632	0.2296	0.0339	0.089
H7B	1	0.8681	0.2706	0.0944	0.089
H7C	1	0.8863	0.3082	−0.0391	0.089
C8	1	0.7200 (3)	0.7401 (2)	0.1340 (2)	0.0440 (5)
C9	1	0.7448 (3)	0.7612 (2)	0.2371 (2)	0.0546 (6)
H9	1	0.7185	0.7081	0.3009	0.065
C10	1	0.8077 (3)	0.8589 (3)	0.2488 (3)	0.0663 (8)
H10	1	0.8249	0.8717	0.3201	0.080
C11	1	0.8451 (3)	0.9372 (3)	0.1579 (3)	0.0697 (8)
H11	1	0.8869	1.0047	0.1662	0.084
C12	1	0.8214 (3)	0.9169 (3)	0.0549 (3)	0.0710 (9)
H12	1	0.8476	0.9705	−0.0085	0.085
C13	1	0.7599 (3)	0.8192 (2)	0.0421 (2)	0.0596 (7)
H13	1	0.7448	0.8061	−0.0301	0.072
C14	1	0.4047 (3)	0.7351 (2)	0.2452 (2)	0.0500 (6)
H14	1	0.4086	0.7930	0.3000	0.060
O15	1	0.3169 (2)	0.7602 (2)	0.1989 (2)	0.0680 (6)
N16	1	0.3227 (2)	0.4850 (2)	0.3002 (2)	0.0391 (4)
N17	1	0.3526 (2)	0.4505 (2)	0.4015 (2)	0.0415 (4)
C18	1	0.4165 (3)	0.3319 (2)	0.4096 (2)	0.0490 (6)
O19	1	0.4752 (2)	0.3037 (2)	0.4786 (2)	0.0682 (6)
O20	1	0.4021 (2)	0.2603 (2)	0.3300 (2)	0.0582 (5)
C21	1	0.4879 (4)	0.1406 (3)	0.3151 (3)	0.0810 (10)
H21A	1	0.5938	0.1433	0.2680	0.097
H21B	1	0.4778	0.1105	0.3953	0.097
C22	1	0.4366 (6)	0.0619 (3)	0.2539 (4)	0.0962 (12)
H22	0.788 (12)	0.4978	−0.0137	0.2253	0.115
H22*	0.212 (12)	0.3964	−0.0030	0.2982	0.115
C23	0.788 (12)	0.3182 (9)	0.0811 (4)	0.2330 (6)	0.105 (3)
H23A	0.788 (12)	0.2526	0.1550	0.2594	0.127
H23B	0.788 (12)	0.2957	0.0214	0.1910	0.127
C23*	0.212 (12)	0.4323 (36)	0.0679 (21)	0.1491 (15)	0.144 (10)
H23C	0.212 (12)	0.4665	0.1319	0.1001	0.173
H23D	0.212 (12)	0.3947	0.0083	0.1199	0.173
C24	1	0.2946 (3)	0.5283 (2)	0.5053 (2)	0.0438 (5)
O25	1	0.2899 (2)	0.4984 (2)	0.6028 (2)	0.0619 (5)
O26	1	0.2446 (2)	0.63688 (15)	0.48078 (14)	0.0464 (4)
C27	1	0.1817 (3)	0.7221 (3)	0.5854 (2)	0.0592 (7)
H27A	0.685 (11)	0.2584	0.7364	0.6151	0.071

H27B	0.685 (11)	0.1010	0.6924	0.6519	0.071
H27C	0.315 (11)	0.2486	0.7119	0.6297	0.071
H27D	0.315 (11)	0.0862	0.7006	0.6399	0.071
C28	0.685 (11)	0.1239 (8)	0.8331 (5)	0.5398 (6)	0.080 (2)
H28	0.685 (11)	0.0444	0.8317	0.5144	0.096
C29	0.685 (11)	0.1766 (9)	0.9322 (5)	0.5329 (6)	0.109 (3)
H29A	0.685 (11)	0.2561	0.9359	0.5577	0.130
H29B	0.685 (11)	0.1356	1.0007	0.5030	0.130
C28*	0.315 (11)	0.1556 (16)	0.8501 (8)	0.5611 (17)	0.095 (5)
H28*	0.315 (11)	0.2330	0.8840	0.5028	0.114
C29*	0.315 (11)	0.0284 (19)	0.9166 (10)	0.6183 (17)	0.150 (8)
H29C	0.315 (11)	−0.0494	0.8833	0.6767	0.181
H29D	0.315 (11)	0.0131	0.9988	0.6018	0.181
S30	1	0.16686 (6)	0.45706 (6)	0.29410 (5)	0.0455 (2)
O31	1	0.0979 (2)	0.3947 (2)	0.39964 (14)	0.0506 (4)
O32	1	0.2009 (2)	0.4029 (2)	0.17757 (15)	0.0623 (5)
C33	1	0.0597 (3)	0.5973 (3)	0.3049 (2)	0.0556 (7)
H33A	1	−0.0310	0.5880	0.2938	0.083
H33B	1	0.1159	0.6470	0.2423	0.083
H33C	1	0.0339	0.6357	0.3848	0.083

Table S2: Anisotropic displacement parameters ($\text{\AA}^2$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	0.0339 (12)	0.0474 (13)	0.0343 (11)	−0.0097 (10)	−0.0103 (9)	0.0048 (9)
C2	0.0449 (14)	0.0439 (13)	0.0414 (12)	−0.0069 (10)	−0.0126 (10)	−0.0023 (10)
C3	0.0421 (14)	0.0476 (14)	0.0375 (12)	−0.0054 (10)	−0.0107 (10)	0.0036 (10)
C4	0.0354 (12)	0.0518 (14)	0.0383 (12)	−0.0050 (10)	−0.0093 (10)	0.0031 (10)
C5	0.0357 (12)	0.0473 (13)	0.0369 (11)	−0.0085 (10)	−0.0113 (9)	0.0080 (10)
C6	0.0336 (12)	0.0438 (13)	0.0358 (11)	−0.0061 (9)	−0.0093 (9)	0.0046 (9)
C7	0.051 (2)	0.054 (2)	0.060 (2)	0.0006 (13)	−0.0109 (13)	−0.0037 (13)
C8	0.0338 (12)	0.0447 (13)	0.0463 (13)	−0.0070 (10)	−0.0073 (10)	0.0071 (10)
C9	0.053 (2)	0.056 (2)	0.060 (2)	−0.0173 (13)	−0.0251 (13)	0.0116 (13)
C10	0.063 (2)	0.061 (2)	0.081 (2)	−0.0183 (15)	−0.031 (2)	−0.001 (2)
C11	0.056 (2)	0.052 (2)	0.091 (2)	−0.0205 (14)	−0.013 (2)	−0.002 (2)
C12	0.067 (2)	0.051 (2)	0.077 (2)	−0.0224 (15)	−0.003 (2)	0.0143 (15)
C13	0.059 (2)	0.058 (2)	0.0518 (15)	−0.0162 (13)	−0.0079 (13)	0.0117 (13)
C14	0.0390 (14)	0.0464 (14)	0.0555 (15)	−0.0100 (11)	−0.0072 (12)	0.0052 (11)
O15	0.0573 (13)	0.0581 (12)	0.0896 (15)	−0.0008 (9)	−0.0329 (11)	0.0129 (11)
N16	0.0343 (10)	0.0498 (11)	0.0349 (9)	−0.0109 (8)	−0.0138 (8)	0.0063 (8)
N17	0.0403 (11)	0.0484 (11)	0.0382 (10)	−0.0104 (9)	−0.0167 (8)	0.0113 (8)
C18	0.0388 (13)	0.0529 (15)	0.0491 (14)	−0.0094 (11)	−0.0095 (11)	0.0111 (12)
O19	0.0585 (12)	0.0802 (14)	0.0640 (12)	0.0020 (10)	−0.0271 (10)	0.0216 (10)
O20	0.0531 (11)	0.0423 (10)	0.0744 (12)	−0.0062 (8)	−0.0199 (9)	0.0059 (9)
C21	0.072 (2)	0.045 (2)	0.109 (3)	−0.0026 (15)	−0.019 (2)	0.005 (2)
C22	0.118 (4)	0.058 (2)	0.103 (3)	−0.017 (2)	−0.031 (3)	0.003 (2)
C23	0.154 (7)	0.063 (3)	0.134 (6)	−0.018 (3)	−0.093 (6)	0.002 (3)
C24	0.0392 (13)	0.0574 (15)	0.0403 (12)	−0.0180 (11)	−0.0175 (10)	0.0101 (11)
O25	0.0784 (14)	0.0730 (13)	0.0448 (10)	−0.0223 (11)	−0.0317 (10)	0.0144 (9)
O26	0.0441 (10)	0.0536 (10)	0.0413 (9)	−0.0077 (8)	−0.0163 (7)	0.0019 (7)
C27	0.049 (2)	0.071 (2)	0.0543 (15)	−0.0124 (13)	−0.0137 (12)	−0.0141 (13)
C28	0.079 (4)	0.063 (3)	0.098 (4)	0.011 (3)	−0.043 (3)	−0.032 (3)
C29	0.165 (8)	0.070 (4)	0.097 (5)	−0.023 (4)	−0.056 (5)	−0.004 (3)
S30	0.0373 (3)	0.0617 (4)	0.0385 (3)	−0.0147 (3)	−0.0131 (3)	0.0030 (3)
O31	0.0408 (10)	0.0627 (11)	0.0467 (9)	−0.0190 (8)	−0.0115 (8)	0.0096 (8)
O32	0.0533 (11)	0.0951 (15)	0.0413 (9)	−0.0256 (10)	−0.0156 (8)	−0.0079 (9)
C33	0.0401 (14)	0.075 (2)	0.0555 (15)	−0.0093 (12)	−0.0228 (12)	0.0190 (13)

Table S3: Geometric parameters (Å², °)

C1–C2	1.499 (3)	C18–O20	1.324 (3)
C1–N16	1.500 (3)	O20–C21	1.456 (3)
C1–C6	1.529 (3)	C21–C22	1.429 (5)
C1–H1	1.00	C21–H21A	0.99
C2–C3	1.331 (3)	C21–H21B	0.99
C2–H2	0.95	C22–C23*	1.274 (7)
C3–C7	1.502 (3)	C22–C23	1.277 (7)
C3–C4	1.502 (3)	C22–H22	0.95
C4–C5	1.530 (3)	C22–H22*	0.95
C4–H4A	0.99	C23–H23A	0.95
C4–H4B	0.99	C23–H23B	0.95
C5–C8	1.515 (3)	C23*–H23C	0.95
C5–C6	1.551 (3)	C23*–H23D	0.95
C5–H5	1.00	C24–O25	1.199 (3)
C6–C14	1.503 (3)	C24–O26	1.325 (3)
C6–H6	1.00	O26–C27	1.463 (3)
C7–H7A	0.98	C27–C28*	1.478 (7)
C7–H7B	0.98	C27–C28	1.484 (6)
C7–H7C	0.98	C27–H27A	0.99
C8–C9	1.381 (3)	C27–H27B	0.99
C8–C13	1.389 (3)	C27–H27C	0.99
C9–C10	1.388 (4)	C27–H27D	0.99
C9–H9	0.95	C28–C29	1.301 (10)
C10–C11	1.373 (4)	C28–H28	0.95
C10–H10	0.95	C29–H29A	0.95
C11–C12	1.371 (4)	C29–H29B	0.95
C11–H11	0.95	C28*–C29*	1.297 (7)
C12–C13	1.383 (4)	C28*–H28*	0.95
C12–H12	0.95	C29*–H29C	0.95
C13–H13	0.95	C29*–H29D	0.95
C14–O15	1.198 (3)	S30–O31	1.428 (2)
C14–H14	0.95	S30–O32	1.428 (2)
N16–N17	1.395 (2)	S30–C33	1.743 (3)
N16–S30	1.654 (2)	C33–H33A	0.98
N17–C24	1.407 (3)	C33–H33B	0.98
N17–C18	1.411 (3)	C33–H33C	0.98
C18–O19	1.195 (3)		

C2-C1-N16	111.9 (2)	O19-C18-O20	126.6 (2)
C2-C1-C6	113.2 (2)	O19-C18-N17	123.5 (3)
N16-C1-C6	109.5 (2)	O20-C18-N17	109.9 (2)
C2-C1-H1	107.3	C18-O20-C21	114.2 (2)
N16-C1-H1	107.3	C22-C21-O20	109.9 (3)
C6-C1-H1	107.3	C22-C21-H21A	109.7
C3-C2-C1	124.5 (2)	O20-C21-H21A	109.7
C3-C2-H2	117.7	C22-C21-H21B	109.7
C1-C2-H2	117.7	O20-C21-H21B	109.7
C2-C3-C7	122.3 (2)	H21A-C21-H21B	108.2
C2-C3-C4	121.4 (2)	C23*-C22-C21	129.4 (9)
C7-C3-C4	116.3 (2)	C23-C22-C21	127.7 (4)
C3-C4-C5	112.5 (2)	C23-C22-H22	116.2
C3-C4-H4A	109.1	C21-C22-H22	116.2
C5-C4-H4A	109.1	C23*-C22-H22*	114.6
C3-C4-H4B	109.1	C21-C22-H22*	115.9
C5-C4-H4B	109.1	C22-C23-H23A	120.0
H4A-C4-H4B	107.8	C22-C23-H23B	120.0
C8-C5-C4	111.1 (2)	H23A-C23-H23B	120.0
C8-C5-C6	113.5 (2)	C22-C23*-H23C	120.0
C4-C5-C6	109.2 (2)	C22-C23*-H23D	120.0
C8-C5-H5	107.6	H23C-C23*-H23D	120.0
C4-C5-H5	107.6	O25-C24-O26	125.3 (2)
C6-C5-H5	107.6	O25-C24-N17	123.7 (2)
C14-C6-C1	111.6 (2)	O26-C24-N17	111.0 (2)
C14-C6-C5	108.8 (2)	C24-O26-C27	113.7 (2)
C1-C6-C5	109.2 (2)	O26-C27-C28*	116.9 (8)
C14-C6-H6	109.1	O26-C27-C28	104.5 (3)
C1-C6-H6	109.1	O26-C27-H27A	110.8
C5-C6-H6	109.1	C28-C27-H27A	110.8
C3-C7-H7A	109.5	O26-C27-H27B	110.8
C3-C7-H7B	109.5	C28-C27-H27B	110.8
H7A-C7-H7B	109.5	H27A-C27-H27B	108.9
C3-C7-H7C	109.5	O26-C27-H27C	108.1
H7A-C7-H7C	109.5	C28*-C27-H27C	108.1
H7B-C7-H7C	109.5	O26-C27-H27D	108.1
C9-C8-C13	118.2 (2)	C28*-C27-H27D	108.1
C9-C8-C5	121.7 (2)	H27C-C27-H27D	107.3
C13-C8-C5	120.0 (2)	C29-C28-C27	123.3 (7)
C8-C9-C10	121.0 (3)	C29-C28-H28	118.3
C8-C9-H9	119.5	C27-C28-H28	118.3
C10-C9-H9	119.5	C28-C29-H29A	120.0
C11-C10-C9	120.2 (3)	C28-C29-H29B	120.0
C11-C10-H10	119.9	H29A-C29-H29B	120.0
C9-C10-H10	119.9	C29*-C28*-C27	120.8 (9)
C12-C11-C10	119.3 (3)	C29*-C28*-H28*	119.6
C12-C11-H11	120.3	C27-C28*-H28*	119.6
C10-C11-H11	120.3	C28*-C29*-H29C	120.0
C11-C12-C13	120.8 (3)	C28*-C29*-H29D	120.0
C11-C12-H12	119.6	H29C-C29*-H29D	120.0
C13-C12-H12	119.6	O31-S30-O32	119.55 (11)
C12-C13-C8	120.5 (3)	O31-S30-N16	106.34 (9)
C12-C13-H13	119.8	O32-S30-N16	108.00 (10)
C8-C13-H13	119.8	O31-S30-C33	108.95 (12)
O15-C14-C6	124.7 (2)	O32-S30-C33	108.10 (13)
O15-C14-H14	117.7	N16-S30-C33	104.95 (11)
C6-C14-H14	117.7	S30-C33-H33A	109.5
N17-N16-C1	119.0 (2)	S30-C33-H33B	109.5
N17-N16-S30	117.71 (14)	H33A-C33-H33B	109.5
C1-N16-S30	121.47 (14)	S30-C33-H33C	109.5
N16-N17-C24	119.2 (2)	H33A-C33-H33C	109.5
N16-N17-C18	121.0 (2)	H33B-C33-H33C	109.5
C24-N17-C18	118.9 (2)		

N16-C1-C2-C3	-133.9 (2)	C6-C1-N16-S30	137.7 (2)
C6-C1-C2-C3	-9.6 (3)	C1-N16-N17-C24	109.5 (2)
C1-C2-C3-C7	176.0 (2)	S30-N16-N17-C24	-85.7 (2)
C1-C2-C3-C4	-3.8 (3)	C1-N16-N17-C18	-81.9 (3)
C2-C3-C4-C5	-17.3 (3)	S30-N16-N17-C18	82.8 (2)
C7-C3-C4-C5	162.8 (2)	N16-N17-C18-O19	162.1 (2)
C3-C4-C5-C8	175.8 (2)	C24-N17-C18-O19	-29.3 (3)
C3-C4-C5-C6	49.8 (2)	N16-N17-C18-O20	-17.3 (3)
C2-C1-C6-C14	162.2 (2)	C24-N17-C18-O20	151.2 (2)
N16-C1-C6-C14	-72.2 (2)	O19-C18-O20-C21	-10.3 (4)
C2-C1-C6-C5	42.0 (2)	N17-C18-O20-C21	169.2 (2)
N16-C1-C6-C5	167.6 (2)	C18-O20-C21-C22	164.7 (3)
C8-C5-C6-C14	50.9 (3)	O20-C21-C22-C23*	60.1 (21)
C4-C5-C6-C14	175.6 (2)	O20-C21-C22-C23	-12.4 (7)
C8-C5-C6-C1	172.9 (2)	N16-N17-C24-O25	165.3 (2)
C4-C5-C6-C1	-62.5 (2)	C18-N17-C24-O25	-3.5 (3)
C4-C5-C8-C9	-69.7 (3)	N16-N17-C24-O26	-13.8 (3)
C6-C5-C8-C9	53.9 (3)	C18-N17-C24-O26	177.4 (2)
C4-C5-C8-C13	107.9 (2)	O25-C24-O26-C27	0.5 (3)
C6-C5-C8-C13	-128.5 (2)	N17-C24-O26-C27	179.6 (2)
C13-C8-C9-C10	0.1 (4)	C24-O26-C27-C28*	166.2 (7)
C5-C8-C9-C10	177.7 (2)	C24-O26-C27-C28	-176.1 (3)
C8-C9-C10-C11	0.6 (5)	O26-C27-C28-C29	-114.9 (6)
C9-C10-C11-C12	-0.8 (5)	C28*-C27-C28-C29	14.8 (19)
C10-C11-C12-C13	0.3 (5)	O26-C27-C28*-C29*	129.4 (17)
C11-C12-C13-C8	0.4 (5)	C28-C27-C28*-C29*	72.8 (21)
C9-C8-C13-C12	-0.6 (4)	N17-N16-S30-O31	-2.7 (2)
C5-C8-C13-C12	-178.2 (3)	C1-N16-S30-O31	161.6 (2)
C1-C6-C14-O15	-28.9 (3)	N17-N16-S30-O32	-132.2 (2)
C5-C6-C14-O15	91.6 (3)	C1-N16-S30-O32	32.2 (2)
C2-C1-N16-N17	68.2 (2)	N17-N16-S30-C33	112.7 (2)
C6-C1-N16-N17	-58.2 (2)	C1-N16-S30-C33	-83.0 (2)
C2-C1-N16-S30	-96.0 (2)		