SUPPORTING INFORMATION

Doubly Activated Cyclopropanes as Synthetic Precursors for the Preparation of 4-Nitro- and 4-Cyano-Dihydropyrroles and Pyrroles.

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General: All phenyliodonium ylide reactions were run in round-bottomed flasks open to air or loosely stoppered with a septum in the case of volatile alkenes. Diazo-mediated cyclopropanation reactions were performed in anhydrous CH_2Cl_2 under an argon atmosphere using standard techniques to prevent introduction of moisture.¹ Anhydrous CH_2Cl_2 was obtained by filtration through drying columns on a GlassContour system (Irvine, CA). Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel (Merck 60 F254). Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate or potassium permanganate. Flash column chromatography was performed using 230-400 mesh silica (EM Science or Silicycle²) of the indicated solvent system according to standard technique.³

Materials: Benzoylnitromethane (**5c**), benzoylacetonitrile (**8a**) and iodobenzene diacetate ($\text{PhI}(\text{OAc})_2$) were purchased from the Aldrich Chemical Company. $[\text{Rh}(\text{Oct})_2]_2$ was purchased from Strem Chemicals. All the alkene and amine substrates used are commercially available from the Aldrich Chemical Company. Styrene was distilled prior to use while 4-fluorostyrene, 1-vinylnaphthalene and 4-phenyl-1-butene were used directly without further purification. The synthesis of α -nitroketones **5a-b**⁴ and **5d**⁵ have

(1) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; 2nd Edition; Wiley: New York, 1986.

(2) This silica gel is preferable for the acid sensitive 1-nitro-1-cyclopropylketones.

(3) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

(4) Charette, A. B.; Wurz, R. P.; Ollevier, T. *Helv. Chim. Acta* **2002**, *85*, 4468-4484.

(5) Wurz, R. P.; Charette, A. B. *Org. Lett.* **2003**, *5*, 2327-2329.

been previously described and were prepared according to the method of Baker and Putt.⁶ α -Nitro- α -diazoketones **4a-c** have been previously described.^{4,7}

4d

1-Cyclopropyl-2-nitro-2-diazo-ethanone (4d). Prepared according to the standard diazo transfer procedure.⁴ Pale yellow solid (273 mg, 80%): M.p. 54-55 °C; R_f 0.67 (30% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 3.13-3.19 (m, 1H), 1.30-1.34 (m, 2H), 1.16-1.21 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.7, 18.8, 13.5; IR (solid) 2151 (CN_2), 1644 (C=O), 1512, 1306 (NO_2) cm^{-1} ; HRMS (EI^+) calcd for $\text{C}_5\text{H}_5\text{N}_3\text{O}_3$ [$\text{M}+1$] $^+$: 156.0332, found: 156.0396.

Typical Experimental Procedure for $[\text{Rh}(\text{Oct})_2]_2$ Catalyzed Cyclopropanation of Alkenes with α -Nitro- α -Diazoketones. Styrene (607 mg, 5.8 mmol, 0.67 mL, 2.0 equiv) was added to a 10 mL round-bottomed flask containing the required amount of $[\text{Rh}(\text{Oct})_2]_2$ catalyst (11.3 mg, 1.5×10^{-3} mmol, 0.5 mol%). 1-Nitro-1-diazopropan-2-one (**4a**, 376 mg, 2.9 mmol, 1.0 equiv) was dissolved in anhydrous CH_2Cl_2 (2.9 mL, 1.0 M) and added slowly dropwise (over *ca.* 20-30 min) to a rapidly stirring solution of styrene and the catalyst allowing for a controlled rate of N_2 evolution. CH_2Cl_2 (0.5 mL) was then used to rinse the flask containing the diazo compound to ensure complete transfer of material. The reaction was allowed to stir 2-4 h, then concentrated under reduced pressure. The diastereoselectivities of the cyclopropanation reaction was determined by ^1H NMR of the crude reaction mixture. Purification by chromatography on silica gel first eluting with hexane (to remove excess olefin) then 5% EtOAc/Hexane afforded **6a** as a clear colorless oil (460 mg, 77%) in a 78:22 *E:Z* ratio which crystallized upon standing. Separation of the diastereomers is possible using a less polar eluent (3% EtOAc/Hexane).

Typical Experimental Procedure for $[\text{Rh}(\text{Oct})_2]_2$ Catalyzed Cyclopropanation of Alkenes with α -Nitroketones and Iodobenzene Diacetate ($\text{PhI}(\text{OAc})_2$). Styrene (1.00 g, 1.1 mL, 9.7 mmol, 5.0 equiv) was added to a 25 mL round-bottomed flask containing the required amount of $[\text{Rh}(\text{Oct})_2]_2$ catalyst (7.5 mg, 9.7×10^{-3} mmol, 0.5 mol%) and

(6) Baker, D. C.; Putt S. R. *Synthesis* **1978**, 478-479.

(7) Charette, A. B.; Wurz, R. P.; Ollevier, T. *J. Org. Chem.* **2000**, 65, 9252-9254.

benzoylnitromethane **5c** (320 mg, 1.9 mmol, 1.0 equiv). Iodobenzene diacetate (687 mg, 2.1 mmol, 1.1 equiv) was then added in one portion and the mixture allowed to stir for 3 h at 40 °C in an oil bath open to air. The crude reaction mixture was then chromatographed directly on silica gel (Silicycle) first using hexane as an eluent (to remove excess alkene) then 5% EtOAc/Hexane affording **6c** as a white crystalline solid (389 mg, 75%) in a 10:90 *E:Z* ratio of the two diastereomers as determined by ¹H NMR. Cyclopropanes **6a-d** have been previously reported.^{4,5}

1-[1-Nitro-(2-(4-fluoro-phenyl)-cyclopropyl)]-ethanone (6e). (405 mg, 63%): *E*-**1-[1-Nitro-(2-(4-fluoro-phenyl)-cyclopropyl)]-ethanone (6e)**. White crystalline solid: M.p. 70 °C; *R_f* 0.34 (10% EtOAc/Hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.11-7.14 (m, 2H), 6.99-7.04 (m, 2H), 3.80 (t, *J* = 10.0 Hz, 1H), 2.55 (dd, *J* = 9.3, 6.4 Hz, 1H), 2.22 (dd, *J* = 10.6, 6.4 Hz, 1H), 2.13 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 193.6, 162.8 (d, *J* = 248.3 Hz, 1C), 130.4, 130.3, 116.2, 115.9, 77.4, 36.6, 29.2, 20.6; IR (solid) 1716 (C=O), 1513, 1347 (NO₂) 1224 cm⁻¹; HRMS (EI⁺) calcd for C₁₁H₁₀NO₃F [M]⁺: 223.06447, found: 223.06525; *Z*-**1-[1-Nitro-(2-(4-fluorophenyl)-cyclopropyl)]-ethanone (6e)**. Clear colorless oil: *R_f* 0.21 (10% EtOAc/Hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.16-7.20 (m, 2H), 6.99-7.03 (m, 2H), 3.53 (t, *J* = 9.6 Hz, 1H), 2.68 (dd, *J* = 9.3, 6.5 Hz, 1H), 2.51 (s, 3H), 2.01 (dd, *J* = 9.8, 6.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 197.1, 163.1 (d, *J* = 248.2 Hz, 1C), 130.6, 130.5, 116.1, 115.8, 36.0, 27.8, 22.9; IR (film) 1710 (C=O), 1537, 1514, 1360 (NO₂), 1228 cm⁻¹; Elem. Anal. calcd for C₁₁H₁₀NO₃F: C 59.19, H 4.52, N 6.28; found: C 59.32, H 4.47, N 6.30.

1-(2-Naphthalen-1-yl-1-nitro-cyclopropyl)-ethanone (6f). (155 mg, 52%): *E*-**1-(2-Naphthalen-1-yl-1-nitro-cyclopropyl)-ethanone (6f)**. White crystalline solid: M.p. 118-

120 °C; R_f 0.68 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.79-7.84 (m, 3H), 7.58 (s, 1H), 7.50-7.52 (m, 2H), 7.28 (d, J = 8.5 Hz, 1H), 3.98 (t, J = 10.0 Hz, 1H), 2.73 (dd, J = 9.3, 6.4 Hz, 1H), 2.29 (dd, J = 10.5, 6.4 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 193.6, 133.2, 133.1, 128.7, 128.1, 127.8, 127.7, 126.84, 126.79, 126.1, 77.2, 37.4, 29.1, 20.5; IR (solid) 1708 (C=O), 1529, 1348 (NO_2), 823, 759 cm^{-1} ; HRMS (EI^+) calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_3$ $[\text{M}]^+$: 255.08954, found: 255.08931; **Z-1-(2-Naphthalen-1-yl-1-nitro-cyclopropyl)-ethanone (6f)**. Clear colorless oil: R_f 0.56 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.78-7.93 (m, 3H), 7.67 (s, 1H), 7.42-7.57 (m, 2H), 7.27-7.33 (m, 1H), 3.68-3.77 (m, 1H), 2.87 (dd, J = 9.3, 6.4 Hz, 1H), 2.10 (dd, J = 9.4, 6.1 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 197.2, 133.2, 136.4, 128.1, 127.91, 127.86, 127.0, 126.8, 126.7, 126.3, 84.5, 37.1, 36.5, 27.8, 22.9, 15.6; Elem. Anal. calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_3$: C 70.58, H 5.13, N 5.49; found: C 70.17, H 5.33, N 5.15.

1-(1-Nitro-2-phenethyl-cyclopropyl)-ethanone (6g). Clear colorless oil (81 mg, 36%); **E-1-(1-nitro-2-phenethyl-cyclopropyl)-ethanone (6g)**. R_f 0.52 (10% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.32 (m, 2H), 7.22-7.24 (m, 1H), 7.14-7.16 (m, 2H), 2.43-2.72 (m, 4H), 2.38 (s, 3H), 1.83 (d, J = 9.9 Hz, 1H), 1.76-1.77 (m, 1H), 1.59-1.61 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 196.0, 140.4, 128.8, 128.64, 128.57, 76.1, 35.2, 33.8, 29.2, 28.5, 23.7; IR (film) 1713 (C=O), 1538, 1355 (NO_2) cm^{-1} ; Elem. Anal. calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$: C 66.94, H 6.48, N 6.00; found: C 66.87, H 6.49, N 5.99; **Z-1-(1-nitro-2-phenethyl-cyclopropyl)-ethanone (6g)**. R_f 0.41 (10% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.31 (m, 2H), 7.21-7.22 (m, 1H), 7.14-7.16 (m, 2H), 2.73-2.75 (m, 2H), 2.43 (s, 3H), 1.87-1.91 (m, 1H), 1.89 (dd, J = 8.9, 5.9 Hz, 1H), 1.70-1.83 (m, 1H), 1.66 (dd, J = 9.7, 6.0 Hz, 1H), 1.57-1.64 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 197.7, 140.6, 128.8, 128.6, 126.5, 79.0, 34.5, 31.8, 29.9, 27.3, 25.1; IR (film) 1709 (C=O), 1532, 1360 (NO_2) cm^{-1} .

Diazo compounds **7a-d** were prepared according to previously reported procedure.⁸

(8) Wurz, R. P.; Lin, W.; Charette, A. B. *Tetrahedron Lett.* **2003**, *44*, 8845-8848.

7b

2-Diazo-3-oxo-4-phenylbutanenitrile (7b). Yellow crystalline solid (136 mg, 84%): M.p. 50-52 °C; R_f 0.46 (CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.39 (m, 5H), 3.88 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.6, 132.1, 129.6, 129.0, 127.8, 108.6, 58.0 (CN_2), 45.9; IR (solid) 2223 (CN), 2139 (CN_2), 1672 (C=O), 1347, 1194, 720 cm^{-1} .

7c

2-Diazo-3-(4-methoxyphenyl)-3-oxopropanenitrile (7c). Yellow crystalline solid (120 mg, 91%): M.p. 62 °C; R_f 0.74 (CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.87 (d, J = 9.1 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 3.82 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 181.1, 164.1, 130.5, 127.4, 114.1, 109.8, 58.4 (CN_2), 55.6; IR (solid) 2221 (CN), 2138 (CN_2), 1628, 1595 (C=O), 1324, 1268, 1250, 1169, 1022, 927, 834, 745 cm^{-1} .

Typical Procedure for the $[\text{Rh}(\text{Oct})_2]_2$ Catalyzed Cyclopropanation of Styrene with α -Cyano- α -Diazoketones. Styrene (137 mg, 1.32 mmol, 0.15 mL, 2.0 equiv) was added to a 10 mL round-bottomed flask containing the required amount of $[\text{Rh}(\text{Oct})_2]_2$ catalyst (2.6 mg, 3.3×10^{-3} mmol, 0.5 mol%). 2-Diazo-3-phenyl-3-oxopropanenitrile (**8a**, 113 mg, 0.66 mmol, 1.0 equiv) was dissolved in anhydrous CH_2Cl_2 (0.66 mL, 1.0 M) and added slowly dropwise (over *ca.* 15-20 min) to the solution containing the alkene and catalysts allowing for a controlled rate of N_2 evolution. CH_2Cl_2 (0.5 mL) was then used to rinse the flask containing the diazo compound to ensure complete transfer of material. The reaction was allowed to stir 2-4 h, then concentrated under reduced pressure. The diastereoselectivity of the cyclopropanation reaction was determined by ^1H NMR of the crude reaction mixture. Purification by chromatography on silica gel, first eluting with hexane (to remove excess olefin) then 5-10% EtOAc/Hexane afforded **9a** as a clear viscous oil (155 mg, 95%) in a 88:12 *E:Z* ratio.

Typical Procedure for $[\text{Rh}(\text{Oct})_2]_2$ Catalyzed Cyclopropanation of Styrene with α -Cyanomethylketones and Iodobenzene Diacetate ($\text{PhI}(\text{OAc})_2$). Styrene (373 mg, 3.58

mmol, 0.41 mL, 5.0 equiv) was added to a 25 mL round-bottomed flask containing the required amount of $[\text{Rh}(\text{Oct})_2]_2$ catalyst (2.8 mg, 3.58×10^{-3} mmol, 0.5 mol%), benzoyl acetonitrile (**8a**, 104 mg, 0.72 mmol, 1.0 equiv), anhydrous Na_2CO_3 (175 mg, 1.65 mmol, 2.3 equiv), oven-dried 4 Å MS (105 mg) and iodobenzene diacetate (254 mg, 0.79 mmol, 1.1 equiv). Anhydrous CH_2Cl_2 (0.72 mL) was then added and the suspension was allowed to stir for 18 h at room temperature under an argon atmosphere. The crude reaction mixture was then filtered through a cotton plug and chromatographed on silica gel, first eluting with hexane (to remove excess olefin) then with 4-8% EtOAc/Hexane affording **1-Benzoyl-2-phenyl-cyclopropane carbonitrile (9a)**. Pale yellow solid (156 mg, 88%): M.p. 79-80 °C (E/Z mix); **E-1-Benzoyl-2-phenyl-cyclopropanecarbonitrile (9a)**. R_f 0.38 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.87-7.99 (m, 2H), 7.26-7.65 (m, 8H), 3.16 (t, J = 8.6 Hz, 1H), 2.56 (dd, J = 9.1, 5.2 Hz, 1H), 2.23 (dd, J = 8.3, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.9, 135.7, 133.9, 133.3, 129.1, 129.0, 128.9, 128.4, 118.8, 38.2, 28.9, 22.6; IR (film) 2237 (CN), 1681 (C=O), 1269, 1009, 696 cm^{-1} ; **Z-1-Benzoyl-2-phenyl-cyclopropanecarbonitrile (9a)**. R_f 0.38 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.97-8.01 (m, 2H), 7.36-7.65 (m, 5H) 7.16-7.26 (m, 3H), 3.56 (t, J = 9.0 Hz, 1H), 2.81 (dd, J = 8.7, 5.7 Hz, 1H), 2.06 (dd, J = 9.3, 5.7 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.5, 135.7, 133.9, 133.3, 129.1, 129.0, 128.9, 128.4, 120.7, 38.8, 26.3, 18.0; IR (film) (E/Z mix) 2238 (CN), 1671 (C=O), 1271, 1010, 740, 693 cm^{-1} .

9b

3-Oxo-4-phenyl-butyronitrile (8b). Prepared according to Chen and Sieburth.⁹ Orange solid (1.46 g, 82%): M.p. 29 °C; R_f 0.22 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.30-7.40 (m, 3H), 7.19-7.26 (m, 2H), 3.83 (s, 2H), 3.49 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 195.7, 132.2, 129.6, 129.2, 127.9, 114.0, 49.1, 31.4; IR (film) 2259 (CN), 1733 (C=O), 1498, 1455, 1060 cm^{-1} ; **2-Phenyl-1-phenylacetyl-cyclopropane carbonitrile (9b)**. Isolated as an inseparable mixture of diastereomers as a pale yellow solid (118 mg, 64%): M.p. 44-46 °C; R_f 0.52 (20% EtOAc/Hexane); **E-2-Phenyl-1-phenylacetyl-cyclopropane carbonitrile (9b)**. ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.43

(9) Chen, Y.; Sieburth, S. M. *Synthesis* **2002**, 2191-2194.

(m, 6H), 7.20-7.29 (m, 2H), 7.09-7.20 (m, 2H), 4.27 (d, $J = 15.4$ Hz, 1H), 4.19 (d, $J = 15.4$ Hz, 1H), 3.04 (t, $J = 8.6$ Hz, 1H), 2.26 (dd, $J = 9.1, 5.0$ Hz, 1H), 2.11 (dd, $J = 8.4, 5.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.4, 133.1, 132.3, 130.0, 129.0, 128.8, 128.7, 128.3, 127.6, 118.4, 48.4, 39.3, 29.9, 24.3; **Z-2-Phenyl-1-phenylacetyl-cyclopropane carbonitrile (9b)**. ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.43 (m, 6H), 6.98-7.00 (m, 2H), 6.94-6.96 (m, 2H), 4.02 (d, $J = 15.1$ Hz, 1H), 3.93 (d, $J = 15.2$ Hz, 1H), 3.30 (t, $J = 9.2$ Hz, 1H), 2.54 (dd, $J = 9.1, 5.5$ Hz, 1H), 1.99 (dd, $J = 9.4, 5.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.0, 131.5, 130.9, 129.8, 129.4, 128.7, 128.2, 127.4, 120.8, 48.7, 40.5, 27.5, 20.0; IR (solid) (E/Z mix) 2235 (CN), 1706 (C=O), 1496, 1454, 1070 cm^{-1} .

9c

3-(4-Methoxy-phenyl)-3-oxo-propionitrile (8c). Prepared according to Chen and Sieburth.⁹ White crystalline solid (443 mg, 42%): M.p. 117-118 °C; R_f 0.09 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.88 (d, $J = 8.9$ Hz, 2H), 6.97 (d, $J = 8.9$ Hz, 1H), 4.04 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 185.7, 164.9, 131.1, 127.4, 114.5, 114.3, 55.9, 29.2; IR (solid) 2258 (CN), 1686 (C=O), 1596, 1224, 1171, 1011, 848, 814 cm^{-1} ; **1-(4-Methoxy-benzoyl)-2-phenyl-cyclopropane carbonitrile (9c)**. Isolated as an inseparable mixture of diastereomers as a clear viscous oil (241 mg, 72%): **E-1-(4-Methoxy-benzoyl)-2-phenyl-cyclopropane carbonitrile (9c)**. R_f 0.44 (20% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 9.0$ Hz, 2H), 7.34-7.47 (m, 5H), 6.98 (d, $J = 9.0$ Hz, 2H), 3.86 (s, 3H), 3.11 (t, $J = 8.7$ Hz, 1H), 2.52 (dd, $J = 9.1, 5.3$ Hz, 1H), 2.17 (dd, $J = 8.3, 5.3$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 189.5, 164.2, 133.5, 131.6, 131.5, 129.0, 128.7, 128.3, 114.1, 55.7, 37.1, 28.3, 21.8; **Z-1-(4-Methoxy-benzoyl)-2-phenyl-cyclopropane carbonitrile (9c)**. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 9.0$ Hz, 2H), 7.34-7.47 (m, 3H), 7.15-7.20 (m, 2H), 6.89 (d, $J = 9.0$ Hz, 2H), 3.82 (s, 3H), 3.48 (t, $J = 8.9$ Hz, 1H), 2.77 (dd, $J = 8.6, 5.8$ Hz, 1H), 2.00 (dd, $J = 9.3, 5.8$ Hz, 1H); IR (film) (E/Z mix) 2236 (CN), 1668 (C=O), 1598, 1255, 1167 cm^{-1} .

2-Phenyl-1-(3-phenyl-acryloyl)-cyclopropanecarbonitrile (9d). Isolated as an inseparable mixture of diastereomers as a pale yellow oil (115 mg, 67%): ***E*-2-Phenyl-1-(3-phenyl-acryloyl)-cyclopropanecarbonitrile (9d).** R_f 0.48 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.82 (d, J = 15.5 Hz, 1H), 7.15-7.68 (m, 11H), 3.27 (t, J = 8.8 Hz, 1H), 2.37 (dd, J = 9.1, 4.9 Hz, 1H), 2.20 (dd, J = 8.4, 4.9 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 189.2, 146.1, 133.9, 133.6, 131.5, 129.2, 129.1, 129.0, 128.9, 128.4, 121.6, 120.6, 38.9, 30.7, 24.9; ***Z*-2-Phenyl-1-(3-phenyl-acryloyl)-cyclopropanecarbonitrile (9d).** ^1H NMR (400 MHz, CDCl_3) δ 7.15-7.68 (m, 12H), 3.47 (t, J = 9.2 Hz, 1H), 2.65 (dd, J = 8.9, 5.3 Hz, 1H), 2.06 (dd, J = 9.3, 5.3 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 186.0, 145.7, 133.9, 131.7, 131.3, 129.6, 129.2, 128.9, 128.7, 128.4, 121.0, 40.2, 27.7, 20.1; IR (film) (E/Z mix) 2232 (CN), 1677 (C=O), 1603, 1449, 1331, 1076, 975 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{19}\text{H}_{15}\text{NO}$ $[\text{M}+\text{H}]^+$: 274.3 m/z , found: 274.2 m/z .

General Procedure for the Synthesis of 4-Nitro-Dihydro-1*H*-Pyrroles (10 or 14). The cyclopropane (**6** or **13**, 0.30 mmol) was treated with anhydrous toluene (1.0 mL) under an argon atmosphere in a 10 mL round-bottomed flask and the desired amine (0.30 mmol) was added. The reaction vessel was fitted with a reflux condenser and heated to 125-130 $^\circ\text{C}$ resulting in a vigorous reflux. After 1-15 h, the reaction was allowed to cool and the bright yellow residue was purified on silica gel (EM Science) using 5-20% EtOAc/Hexane as an eluent.

5-Methy-4-nitro-1,2-diphenyl-2,3-dihydro-1*H*-pyrrole (10a). Yellow solid (34 mg, 91%): M.p. 134-135 $^\circ\text{C}$; R_f 0.53 (50% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.31 (m, 8H), 6.90-6.93 (m, 2H), 5.17 (dd, J = 11.6, 7.0 Hz, 1H), 3.77 (dd, J = 15.5, 11.7 Hz, 1H), 3.30 (dd, J = 15.5, 7.0 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 140.0, 138.3, 129.7, 129.2, 128.8, 128.4, 127.3, 127.0, 123.3, 69.4, 36.8, 15.7;

IR (solid) 1557, 1379, 1362, 1262, 1170 cm^{-1} ; HRMS (EI^+) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$ [M] $^+$: 280.12118, found: 280.12085; Elem. Anal. calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$: C 72.84, H 5.75, N 9.99; found: C 72.69, H 5.86, N 9.86.

4-Nitro-1,2-diphenyl-5-propyl-2,3-dihydro-1H-pyrrole (10b). Yellow solid (86 mg, 78%); M.p. 155-156 $^{\circ}\text{C}$; R_f 0.12 (20% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.29 (m, 6H), 7.18-7.20 (m, 2H), 6.91-6.92 (m, 2H), 5.08 (dd, $J = 11.7, 7.1$ Hz, 1H), 3.76 (dd, $J = 15.5, 11.8$ Hz, 1H), 3.30 (dd, $J = 15.6, 7.1$ Hz, 1H), 2.80-2.87 (m, 1H), 2.59-2.66 (m, 1H), 1.58-1.69 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.8, 140.1, 138.2, 129.7, 129.1, 128.8, 128.7, 127.3, 122.3, 69.6, 36.8, 29.5, 21.1, 14.4; IR (solid) 1529, 1505, 1399 (NO_2), 1360, 1265 cm^{-1} ; HRMS (EI^+) calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$ [M] $^+$: 308.15248, found: 308.15284; Elem. Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$: C 74.00, H 6.54, N 9.08; found: C 73.62, H 6.63, N 8.97.

4-Nitro-1,2,5-triphenyl-2,3-dihydro-1H-pyrrole (10c). Yellow solid (96 mg, 91%); M.p. 185-187 $^{\circ}\text{C}$; R_f 0.28 (20% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.41 (m, 10H), 6.97-7.04 (m, 3H), 6.63-6.66 (m, 2H), 5.25 (dd, $J = 11.8, 6.6$ Hz, 1H), 3.98 (dd, $J = 15.6, 11.8$ Hz, 1H), 3.41 (dd, $J = 15.6, 6.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 141.2, 140.1, 130.4, 129.9, 129.4, 129.3, 129.0, 128.8, 128.3, 127.0, 126.7, 123.4, 69.0, 38.3; IR (solid) 1561, 1490, 1365, 1346 (NO_2), 1259 cm^{-1} ; HRMS (EI^+) calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$ [M] $^+$: 342.13683, found: 342.13666; Elem. Anal. calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$: C 77.17, H 5.30, N 8.18; found: C 77.30, H 5.51, N 8.02.

5-Cyclopropyl-4-nitro-1,2-diphenyl-2,3-dihydro-1H-pyrrole (10d). Yellow oil (93 mg, 79%): R_f 0.38 (30% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 6.98-7.36 (m, 8H), 6.92-6.98 (m, 2H), 5.03 (dd, $J = 11.7, 6.2$ Hz, 1H), 3.76 (dd, $J = 15.5, 11.7$ Hz, 1H), 3.20 (dd, $J = 15.5, 6.2$ Hz, 1H), 2.18-2.25 (m, 1H), 1.00-1.06 (m, 1H), 0.87-0.95 (m, 1H), 0.62-0.70; ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 140.9, 140.1, 129.2, 129.1, 128.5, 127.4, 126.8, 125.8, 125.4, 68.9, 37.3, 11.5, 10.6, 9.8; IR (film) 1558, 1407, 1371, 1339 (NO_2), 1256 cm^{-1} ; HRMS (EI^+) calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$ [M] $^+$: 306.13683, found: 306.13666.

5-Cyclopropyl-1-(4-methoxy-phenyl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole (10e). Yellow solid (209 mg, 97%): R_f 0.32 (50% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.22-7.31 (m, 3H), 7.14-7.17 (m, 2H), 6.79-6.83 (m, 2H), 6.69-6.73 (m, 2H), 4.94 (dd, $J = 11.7, 6.6$ Hz, 1H), 3.67-3.80 (m, 1H), 3.71 (s, 3H), 3.20 (dd, $J = 15.6, 6.6$ Hz, 1H), 2.17-2.26 (m, 1H), 0.85-1.02 (m, 2H), 0.67-0.74 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 163.8, 158.7, 140.7, 132.5, 129.0, 128.6, 127.6, 127.0, 124.4, 114.3, 69.4, 55.4, 37.0, 11.3, 10.1, 9.6; IR (solid) 1511, 1368, 1336 (NO_2), 1232, 1161 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$ [$\text{M}+\text{H}$] $^+$: 337.4 m/z , found: 337.2 m/z .

1-Allyl-5-methyl-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole (10f). Yellow oil (16 mg, 48%): R_f 0.05 (20% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.42 (m, 3H), 7.23-7.26 (m, 2H), 5.57-5.64 (m, 1H), 5.26 (d, $J = 9.7$ Hz, 1H), 5.10 (d, $J = 17.1$ Hz, 1H),

4.82 (dd, $J = 11.7, 7.2$ Hz, 1H), 3.90-3.95 (m, 1H), 3.61-3.65 (m, 1H), 3.46-3.53 (m, 1H), 3.12-3.18 (m, 1H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.0, 139.7, 130.8, 129.5, 129.1, 127.3, 118.9, 65.5, 47.4, 36.7, 13.9; IR (film) 1547, 1382 (NO_2), 1249, 1164 cm^{-1} ; HRMS (EI^+): $[\text{M}-2]^+$ $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$: 242.10553, found: 242.10601.

1-Benzyl-5-methyl-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole (10g). Yellow oil (39 mg, 35%): R_f 0.32 (40% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.30-7.42 (m, 6H), 7.18-7.21 (m, 2H), 7.03-7.05 (m, 2H), 4.71 (dd, $J = 11.8, 6.9$ Hz, 1H), 4.63 (d, $J = 16.2$ Hz, 1H), 3.97 (d, $J = 16.2$ Hz, 1H), 3.58 (dd, $J = 15.6, 11.8$ Hz, 1H), 3.14 (dd, $J = 15.6, 6.9$ Hz, 1H), 2.72 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 161.7, 139.5, 134.5, 129.5, 129.4, 129.1, 128.5, 127.2, 65.0, 48.3, 36.5, 14.2; IR (film) 1549, 1379, 1345 (NO_2), 1241, 1164 cm^{-1} ; HRMS (EI^+): $[\text{M}-2]^+$ $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$: 292.12118, found: 292.12139.

5-Methyl-4-nitro-2-phenyl-1-(1-*R*-phenyl-ethyl)-2,3-1H-pyrrole (10h). Yellow oil as a mixture of diastereomers (70 mg, 84%): **1st diastereomer.** R_f 0.29 (40% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.42 (m, 6H), 7.17-6.97 (m, 4H), 4.97-5.02 (m, 1H), 4.59 (dd, $J = 11.7, 5.4$ Hz, 1H), 3.55 (dd, $J = 15.5, 11.7$ Hz, 1H), 3.04 (dd, $J = 15.5, 5.3$ Hz, 1H), 2.67 (s, 3H), 1.27 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.3, 142.0, 138.8, 129.3, 129.2, 128.9, 128.6, 127.0, 126.9, 63.7, 55.6, 37.5, 19.0, 14.7; IR (film) 1549, 1375, 1350 (NO_2), 1258, 1167 cm^{-1} ; HRMS (EI^+): $[\text{M}-2]^+$ $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$: 306.13683, found: 306.13616; **2nd diastereomer.** R_f 0.24 (40% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.09-7.39 (m, 10H), 4.92-4.97 (m, 1H), 4.71-4.73 (m, 1H), 3.68 (dd, $J = 11.8, 3.7$ Hz, 1H), 3.17 (dd, $J = 15.6, 6.4$ Hz, 1H), 2.52 (s, 3H), 1.55 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.6, 140.5, 138.8, 129.3, 129.2, 129.0, 128.8, 127.4, 126.3, 67.7, 56.1, 37.2, 19.0, 15.7; IR (film) (mix of diastereomers) 1542, 1374, 1347 (NO_2), 1248, 1151 cm^{-1} .

1-tert-Butyl-5-methyl-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole (10i). Dark orange oil (78 mg, 47%): R_f 0.12 (50% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.24-7.30 (m, 3H), 7.11-7.14 (m, 2H), 5.03-5.07 (m, 1H), 3.44-3.53 (m, 1H), 2.89 (s, 3H), 2.75-2.81 (m, 1H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.1, 142.8, 129.3, 128.2, 125.2, 121.8, 64.9, 58.5, 37.4, 30.6, 17.6; IR (film) 1527, 1348 (NO_2), 1262, 1163, 999 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 261.3 m/z , found: 261.1 m/z .

1-(4-Chloro-phenyl)-5-methyl-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole (10j). Yellow crystalline solid (81 mg, 95%): M.p. 153-154 $^\circ\text{C}$; R_f 0.28 (30% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.19-7.33 (m, 7H), 6.85-6.90 (m, 2H), 5.13 (dd, $J = 11.6$, 7.3 Hz, 1H), 3.70-3.80 (m, 1H), 3.24-3.32 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 160.1, 139.8, 136.9, 134.1, 130.0, 129.3, 129.0, 128.3, 127.3, 123.7, 69.3, 36.8, 15.6; IR (solid) 1552, 1497, 1346 (NO_2), 1243, 1166 cm^{-1} ; HRMS (EI^+) calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}_2\text{Cl}$ $[\text{M}]^+$: 314.08221, found: 314.08180; Elem. Anal. calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}_2\text{Cl}$: C 64.87, H 4.80, N 8.90; found: C 65.01, H 4.77, N 8.81.

1-(4-Methoxy-phenyl)-4-nitro-2,5-diphenyl-2,3-dihydro-1H-pyrrole (10k). Yellow crystalline solid (96 mg, 96%): M.p. 60-78 $^\circ\text{C}$; R_f 0.41 (40% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.26-7.40 (m, 10H), 6.56-6.61 (m, 2H), 6.48-6.53 (m, 2H), 5.17 (dd,

$J = 11.9, 7.0$ Hz, 1H), 3.95 (dd, $J = 15.6, 11.9$ Hz, 1H), 3.62 (s, 3H), 3.43 (dd, $J = 15.6, 7.0$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.2, 158.1, 141.0, 132.6, 130.1, 129.7, 129.4, 129.3, 128.7, 128.2, 127.9, 127.2, 122.6, 114.1, 69.4, 55.3, 37.9; IR (solid) 1511, 1343 (NO_2), 1236, 1125 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 373.4 m/z , found: 373.1 m/z .

5-Methyl-4-nitro-1-phenyl-2-(4-fluorophenyl)-2,3-dihydro-1H-pyrrole (10l). Yellow glaze (75 mg, 99%): M.p. 43-45 °C; R_f 0.09 (20% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.18-7.33 (m, 5H), 6.90-7.01 (m, 4H), 5.17 (dd, $J = 11.7, 7.2$ Hz, 1H), 3.76 (dd, $J = 15.5, 11.7$ Hz, 1H), 3.27 (dd, $J = 15.5, 7.2$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.8 (d, $J = 248.0$ Hz, 1C), 138.1, 135.8, 129.8, 129.2, 129.1, 128.6, 127.1, 116.3, 116.1, 76.4, 68.9, 36.8, 15.8; IR (film) 1551, 1509, 1356 (NO_2), 1251, 1222, 1152 cm^{-1} ; HRMS (EI^+) calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}_2\text{F}$ $[\text{M}]^+$: 298.11176, found: 298.11112.

5-Methyl-2-naphthalen-1-yl-4-nitro-1-phenyl-2,3-dihydro-1H-pyrrole (10m). Yellow crystalline solid (49 mg, 84%): M.p. 175 °C; R_f 0.13 (50% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.80-7.85 (m, 2H), 7.74-7.76 (m, 1H), 7.58 (s, 1H), 7.46-7.51 (m, 2H), 7.41-7.44 (m, 1H), 7.18-7.28 (m, 3H), 6.92-6.95 (m, 2H), 5.34 (dd, $J = 11.7, 7.0$ Hz, 1H), 3.84 (dd, $J = 15.6, 11.7$ Hz, 1H), 3.38 (dd, $J = 15.6, 7.0$ Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 160.9, 138.3, 137.2, 133.4, 133.2, 129.8, 129.6, 128.4, 128.1, 128.0, 127.0, 126.8, 126.8, 124.1, 69.6, 36.8, 15.8; IR (solid) 1548, 1393, 1346 (NO_2), 1242, 1019 cm^{-1} ; HRMS (EI^+) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_2$ $[\text{M}]^+$: 330.13683, found: 330.13655; Elem. Anal. calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_2$: C 76.34, H 5.49, N 8.48; found: C 76.33, H 5.56, N 8.48.

5-Methyl-4-nitro-2-phenethyl-1-phenyl-2,3-dihydro-1H-pyrrole (10n). Yellow oil (11 mg, 18%): R_f 0.08 (20% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.49 (m, 3H), 7.18-7.27 (m, 3H), 7.04-7.11 (m, 4H), 4.28-4.30 (m, 1H), 3.47 (dd, $J = 14.5, 11.1$ Hz, 1H), 3.10 (d, $J = 15.1, 7.2$ Hz, 1H), 2.67-2.70 (m, 1H), 2.53-2.57 (m, 1H), 2.37 (s, 3H), 1.88-1.92 (m, 1H), 1.76-1.79 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.1, 140.5, 137.7, 130.1, 128.8, 128.4, 127.1, 126.5, 123.7, 64.6, 35.4, 32.8, 30.9, 15.6; IR (film) 1552, 1357 (NO_2), 1258, 1168 cm^{-1} ; HRMS (EI^+) calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$ $[\text{M}]^+$: 308.15248, found: 308.15229.

The synthesis of cyclopropane **11** has been already described.⁵

(1-Nitro-2-phenyl-cyclopropyl)-methanol (12). Prepared according to O'Bannon and Dailey¹⁰ (605 mg, 87%); ***E*-(1-Nitro-2-phenyl-cyclopropyl)-methanol (12).** White solid: M.p. 50-52 °C; R_f 0.21 (20% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.39 (m, 5H), 3.98 (d, $J = 13.9$ Hz, 1H), 3.64 (d, $J = 13.9$ Hz, 1H), 3.56 (t, $J = 9.3$ Hz, 1H), 2.31 (dd, $J = 10.3, 6.2$ Hz, 1H), 1.85 (dd, $J = 8.4, 6.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.7, 129.03, 128.98, 128.4, 70.6, 60.8, 34.8, 20.6; IR (film) 1537, 1351 (NO_2), 1043 cm^{-1} ; ***Z*-(1-Nitro-2-phenyl-cyclopropyl)-methanol (12).** White solid: M.p. 38-39 °C; R_f 0.11 (20% EtOAc/Hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.34 (m, 5H), 4.36 (d, $J = 13.3$ Hz, 1H), 3.96 (d, $J = 13.4$ Hz, 1H), 2.99 (t, $J = 9.3$ Hz, 1H), 2.64 (dd, $J = 8.9, 6.7$ Hz, 1H), 2.05 (s(*br*), 1H), 1.71 (dd, $J = 9.5, 6.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.5, 129.3, 128.7, 128.3, 76.5, 72.7, 65.2, 33.5, 19.2; IR (film) 1529, 1350 (NO_2), 1036 cm^{-1} .

(10) O'Bannon, P. E.; Dailey, W. P. *Tetrahedron* **1990**, *46*, 7341-7358.

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***E*-1-Nitro-2-phenylcyclopropanecarbaldehyde (13).** The oxidation was performed in refluxing EtOAc using IBX (3.0 equiv) as an oxidant according to the procedure reported by More and Finney.¹¹ White crystalline solid (27 mg, 54%): M.p. 80-81 °C; *R_f* 0.53 (20% EtOAc/Hexane); ¹H NMR (400 MHz, CDCl₃) δ 10.26 (s, 1H), 7.22-7.36 (m, 5H), 3.92 (t, *J* = 10.3 Hz, 1H), 2.60-2.70 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 189.2, 130.5, 129.6, 128.9, 128.7, 44.3, 22.9; IR (solid) 1713 (C=O), 1535, 1367, 1344 (NO₂) cm⁻¹.

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1-(4-Chloro-phenyl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole (14). Yellow oil (33 mg, 79%): *R_f* 0.41 (30% EtOAc/Hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.38 (s, 1H), 7.33-7.39 (m, 3H), 7.20-7.32 (m, 4H), 6.88-6.90 (m, 2H), 5.56 (dd, *J* = 11.9, 5.7 Hz, 1H), 3.80-3.87 (m, 1H), 3.12-3.17 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.4, 139.8, 137.9, 130.0, 129.8, 128.9, 125.7, 118.2, 67.1, 37.6; IR (film) 1571, 1367 (NO₂), 1276, 1212 cm⁻¹.

General Procedure for the Synthesis of 4-Cyano-Dihydro-1H-Pyrroles (15). The cyclopropane (**9**, 0.30 mmol) was treated with anhydrous toluene (1.0 mL) under an argon atmosphere in a 10 mL round-bottomed flask and the desired amine (0.30 mmol) was added. The reaction vessel was fitted with a reflux condenser and heated to 125-130 °C resulting in a vigorous reflux of the toluene. After 4-15 h, the reaction was allowed to cool and the residue was purified on silica gel (EM Science) using 5-20% EtOAc/Hexane as an eluent.

(11) More, J. D.; Finney, N. S. *Org. Lett.* **2002**, *4*, 3001-3003.

1-(4-Chloro-phenyl)-5-phenyl-2-styryl-4,5-dihydro-1H-pyrrole-3-carbonitrile (15a).

Yellow solid (66 mg, 82%): M.p. 72-73 °C; R_f 0.37 (10% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.26-7.43 (m, 10H), 7.13-7.18 (m, 2H), 6.80-6.85 (m, 2H), 6.63 (d, J = 16.5 Hz, 1H), 4.99 (dd, J = 11.1, 7.0 Hz, 1H), 3.52 (dd, J = 15.5, 11.1 Hz, 1H), 2.81 (dd, J = 15.4, 7.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 157.2, 142.4, 141.6, 138.7, 135.5, 130.5, 129.7, 129.4, 129.3, 129.1, 128.4, 127.5, 126.6, 125.0, 119.6, 116.0, 81.1, 70.6, 39.4; IR (solid) 2184 (CN), 1490, 1386, 827, 751, 692 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{25}\text{H}_{19}\text{N}_2\text{Cl}$ $[\text{M}+\text{H}]^+$: 383.9 m/z , found: 383.1 m/z .

2-Benzyl-1-(4-chloro-phenyl)-5-phenyl-4,5-dihydro-1H-pyrrole-3-carbonitrile (15b).

Pale yellow oil (121 mg, 91%): R_f 0.40 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.19-7.27 (m, 6H), 7.08-7.15 (m, 4H), 6.97-7.00 (m, 2H), 6.63-6.68 (m, 2H), 4.98 (dd, J = 11.4, 9.3 Hz, 1H), 3.81 (d, J = 15.0 Hz, 1H), 3.63 (d, J = 15.0 Hz, 1H), 3.39 (dd, J = 12.3, 11.4 Hz, 1H), 2.85 (dd, J = 14.6, 10.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 162.9, 141.5, 139.7, 135.9, 132.4, 129.4, 129.0, 128.7, 128.6, 128.3, 128.1, 127.2, 127.1, 119.8, 79.7, 70.8, 38.4, 33.3; IR (film) 2187 (CN), 1593, 1493, 1422, 1188, 824, 724, 696 cm^{-1} .

1,2,5-Triphenyl-4,5-dihydro-1H-pyrrole-3-carbonitrile (15c). Pale yellow solid (127 mg, 97%): M.p. 126-127 °C; R_f 0.68 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.57-7.62 (m, 2H), 7.34-7.46 (m, 8H), 7.01-7.06 (m, 2H), 6.91-6.96 (m, 1H), 6.62-6.65 (m, 2H), 5.12 (d, J = 11.3, 5.6 Hz, 1H), 3.67 (dd, J = 15.0, 11.3 Hz, 1H), 2.84 (dd, J = 15.0, 5.6 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 160.2, 143.4, 143.2, 130.3, 129.9, 129.3, 128.8, 128.7, 128.6, 128.2, 126.1, 124.2, 123.1, 119.7, 81.2, 70.2, 39.6; IR (solid) 2177 (CN), 1661, 1581, 1560, 1493, 1417, 1271 cm^{-1} .

1-(4-Chloro-phenyl)-2,5-diphenyl-4,5-dihydro-1H-pyrrole-3-carbonitrile (15d). White powder (138 mg, 99%): M.p. 178-179 °C; R_f 0.46 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.50-7.57 (m, 2H), 7.34-7.47 (m, 8H), 6.92-7.00 (m, 2H), 6.47-6.55 (m, 2H), 5.08 (d, J = 11.3, 5.8 Hz, 1H), 3.65 (dd, J = 15.1, 11.3 Hz, 1H), 2.83 (dd, J = 15.1, 5.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.8, 143.0, 141.8, 130.5, 129.6, 129.5, 129.4, 129.0, 128.8, 128.6, 128.3, 126.1, 124.3, 119.4, 82.1, 70.2, 39.6; IR (solid) 2177 (CN), 1563, 1492, 1423, 1091 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2\text{Cl}$ $[\text{M}+\text{H}]^+$: 357.9 m/z , found: 357.2 m/z .

2-(4-Methoxy-phenyl)-1,5-diphenyl-4,5-dihydro-1H-pyrrole-3-carbonitrile (15e). White crystalline solid (156 mg, 77%): M.p. 97-98 °C; R_f 0.32 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.51 (d, J = 9.0 Hz, 2H), 7.33-7.45 (m, 5H), 7.00-7.06 (m, 2H), 6.85-6.95 (m, 3H), 6.60 (d, J = 8.5 Hz, 2H), 5.06 (dd, J = 11.1, 5.3 Hz, 1H), 3.82 (s, 3H), 3.63 (dd, J = 14.9, 11.2 Hz, 1H), 2.78 (dd, J = 14.9, 5.3 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 161.1, 160.0, 143.7, 130.3, 129.3, 128.8, 128.2, 126.2, 124.1, 123.2, 122.2, 120.2, 114.3, 80.0, 70.3, 55.5, 39.5; IR (solid) 2188 (CN), 1593, 1510, 1497, 1389,

1254, 1177, 1029 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 353.4 m/z , found: 353.2 m/z .

General Procedure for the Oxidation of Dihydropyrroles (10 or 15) to Pyrroles Using DDQ. In a 50 mL round-bottomed flask the dihydropyrrole **10** or **15** was treated with toluene to make a 0.020 M solution. DDQ (1.5 equiv) was then added in one portion to the reaction mixture and the flask fitted with a reflux condenser under an argon atmosphere. The reaction mixture was heated to reflux in an oil bath for 3 h, cooled to room temperature and diluted with Et_2O (20 mL). The reaction mixture was then treated with a saturated solution of Na_2CO_3 in water (*ca.* 15 mL) and stirred for 20 min. After further treatment with brine (15 mL), the organic layer was removed. The organic layer was then washed with a saturated solution of Na_2CO_3 in water (2x15 mL), dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure (rotary evaporator). The crude residue was recrystallized (EtOAc/Hexane) or purified by column chromatography on silica gel using 5-20% EtOAc/Hexane as an eluent.

3-Nitro-1,2,5-triphenyl-1H-pyrrole (20a). Yellow solid (63 mg, 77%): M.p. 166 $^{\circ}\text{C}$; R_f 0.40 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.15-7.30 (m, 14H), 7.08-7.12 (m, 2H), 6.93-6.97 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 136.9, 135.2, 134.4, 131.2, 131.0, 129.5, 129.04, 129.01, 128.94, 128.88, 128.54, 128.45, 128.0, 127.9, 106.0; IR (solid) 1492, 1396, 1319 (NO_2) cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 341.4 m/z , found: 341.1 m/z .

1,2,5-Triphenyl-1H-pyrrole-3-carbonitrile (20b). White solid (149 mg, 94%): M.p. 217-218 $^{\circ}\text{C}$; R_f 0.44 (20% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.17-7.31 (m, 11H), 7.03-7.09 (m, 2H), 6.95-6.99 (m, 2H), 6.72 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ

142.1, 137.5, 136.3, 131.4, 129.9, 129.6, 129.25, 129.16, 128.8, 128.6, 128.52, 128.48, 128.4, 127.7, 117.4, 112.3, 112.2, 93.7, 77.7; IR (solid) 2228 (CN), 1494, 1190 cm^{-1} .

1-(4-Chloro-phenyl)-5-phenyl-2-styryl-1H-pyrrole-3-carbonitrile (20c). Pale yellow solid (136 mg, 91%): M.p. 197-198 °C; R_f 0.44 (10% EtOAc/Hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.03-7.54 (m, 15H), 6.69 (s, 1H), 6.60 (d, J = 16.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 139.3, 136.6, 136.3, 135.6, 135.2, 133.0, 130.8, 130.2, 129.9, 128.9, 128.7, 128.6, 128.0, 126.9, 117.6, 115.0, 113.3, 113.2, 91.3; IR (solid) 2116 (CN), 1493, 1093, 960, 839 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{25}\text{H}_{17}\text{N}_2\text{Cl}$ $[\text{M}+\text{H}]^+$: 381.9 m/z , found: 381.1 m/z .

7c

ORTEP representation of the crystal structure of 4-nitro-1,2-diphenyl-5-propyl-2,3-dihydro-1*H*-pyrrole (**10b**).

<i>Data collection</i>	
Nonius CAD-4 diffractometer	840 reflections with
$\omega/2\theta$ scan	$>2\sigma(I)$
	$R_{\text{int}} = 0.140$
Absorption correction:	$\theta_{\text{max}} = 69.87^\circ$
by integration ABSORP in <i>NRCVAX</i> (Gabe <i>et al.</i> 1989)	$h = -17 \rightarrow 17$
	$k = -12 \rightarrow 12$
$T_{\text{min}} = 0.8583$, $T_{\text{max}} = 0.9301$	$l = -25 \rightarrow 25$
30400 measured reflections	5 standard reflections
3047 independent reflections	frequency: 60 min
	intensity decay: no decay, variation 4.2%
<i>Refinement</i>	
Refinement on F^2	$w=1/[\sigma^2(F_o^2) + (0.0487P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.0519$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.1199$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.087$	$\Delta\rho_{\text{max}} = 0.164 \text{ e } \text{\AA}^{-3}$
3047 reflections	$\Delta\rho_{\text{min}} = -0.236 \text{ e } \text{\AA}^{-3}$
209 parameters	Extinction correction: none
H-atom parameters constrained	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)

Table 1. *Selected geometric parameters* ($\text{\AA}$, $^\circ$)

N1—C2	1.345 (4)	C14—C15	1.369 (6)
N1—C11	1.434 (5)	C15—C16	1.370 (6)
N1—C5	1.511 (5)	C21—C22	1.533 (5)
C2—C3	1.359 (5)	C22—C23	1.513 (5)
C2—C21	1.514 (5)	N31—O31	1.246 (4)
C3—N31	1.382 (5)	N31—O32	1.269 (4)
C3—C4	1.488 (5)	C51—C56	1.375 (6)
C4—C5	1.542 (5)	C51—C52	1.380 (5)
C5—C51	1.474 (6)	C52—C53	1.361 (6)
C11—C12	1.373 (5)	C53—C54	1.378 (7)
C11—C16	1.393 (5)	C54—C55	1.384 (6)
C12—C13	1.395 (6)	C55—C56	1.365 (6)
C13—C14	1.405 (6)		

C2—N1—C11	128.8 (4)	C12—C13—C14	117.7 (5)
C2—N1—C5	111.1 (3)	C15—C14—C13	121.0 (5)
C11—N1—C5	120.0 (3)	C14—C15—C16	121.2 (5)
N1—C2—C3	110.9 (4)	C15—C16—C11	118.3 (4)
N1—C2—C21	120.0 (4)	C2—C21—C22	112.3 (4)
C3—C2—C21	129.1 (4)	C23—C22—C21	114.1 (4)
C2—C3—N31	128.3 (4)	O31—N31—O32	122.7 (4)
C2—C3—C4	111.3 (4)	O31—N31—C3	118.4 (4)
N31—C3—C4	120.4 (4)	O32—N31—C3	118.9 (4)
C3—C4—C5	103.4 (3)	C56—C51—C52	117.6 (5)
C51—C5—N1	110.6 (4)	C56—C51—C5	122.2 (4)
C51—C5—C4	115.2 (4)	C52—C51—C5	120.2 (4)
N1—C5—C4	102.6 (3)	C53—C52—C51	120.6 (5)
C12—C11—C16	121.6 (4)	C52—C53—C54	121.8 (5)
C12—C11—N1	118.5 (4)	C53—C54—C55	118.0 (5)
C16—C11—N1	119.9 (4)	C56—C55—C54	119.8 (5)
C11—C12—C13	120.2 (5)	C55—C56—C51	122.3 (5)
C11—N1—C2—C3	173.3 (4)	C13—C14—C15—C16	−2.8 (7)
C5—N1—C2—C3	−2.6 (5)	C14—C15—C16—C11	0.4 (7)
C11—N1—C2—C21	−5.1 (7)	C12—C11—C16—C15	1.5 (6)
C5—N1—C2—C21	179.0 (4)	N1—C11—C16—C15	−179.5 (4)
N1—C2—C3—N31	179.7 (5)	N1—C2—C21—C22	107.4 (5)
C21—C2—C3—N31	−2.1 (8)	C3—C2—C21—C22	−70.6 (6)
N1—C2—C3—C4	−3.2 (6)	C2—C21—C22—C23	−61.7 (5)
C21—C2—C3—C4	175.0 (4)	C2—C3—N31—O31	171.8 (5)
C2—C3—C4—C5	7.3 (5)	C4—C3—N31—O31	−5.1 (7)
N31—C3—C4—C5	−175.3 (4)	C2—C3—N31—O32	−6.7 (8)
C2—N1—C5—C51	−116.5 (4)	C4—C3—N31—O32	176.5 (4)
C11—N1—C5—C51	67.3 (5)	N1—C5—C51—C56	63.4 (5)
C2—N1—C5—C4	6.9 (5)	C4—C5—C51—C56	−52.3 (6)
C11—N1—C5—C4	−169.4 (4)	N1—C5—C51—C52	−119.6 (4)
C3—C4—C5—C51	112.2 (4)	C4—C5—C51—C52	124.7 (4)
C3—C4—C5—N1	−8.0 (5)	C56—C51—C52—C53	2.1 (7)
C2—N1—C11—C12	−109.5 (5)	C5—C51—C52—C53	−175.0 (5)
C5—N1—C11—C12	66.0 (5)	C51—C52—C53—C54	−0.9 (8)
C2—N1—C11—C16	71.5 (6)	C52—C53—C54—C55	−0.5 (8)
C5—N1—C11—C16	−113.0 (4)	C53—C54—C55—C56	0.6 (8)
C16—C11—C12—C13	−1.1 (6)	C54—C55—C56—C51	0.7 (8)
N1—C11—C12—C13	179.9 (4)	C52—C51—C56—C55	−2.1 (8)
C11—C12—C13—C14	−1.2 (7)	C5—C51—C56—C55	175.0 (5)
C12—C13—C14—C15	3.1 (7)		

Data collection: CAD-4 software (Enraf-Nonius, 1989). Cell refinement: CAD-4 software (Enraf-Nonius, 1989). Data reduction: NRC-2, NRC-2A (Ahmed *et al.* 1973). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: *SHELXL96* (Sheldrick, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference:). Services for accessing these data are described at the back of the journal.

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Fig. 1 *ORTEP* (*SHELXTL* (1997)) drawing of the molecule. Ellipsoids correspond to 40% probability.

Space group confirmed by *PLATON* program (Spek, 1995). Data reduction performed using a locally modified version of the NRC-2 program (Ahmed *et al.* 1973). The structure was solved by direct method using *SHELXS97* (Sheldrick, 1997) and difmap synthesis using *SHELXTL* (Sheldrick, 1997) and *SHELXL96* (Sheldrick, 1996). All non-H atoms anisotropic, H atoms isotropic. H atoms constrained to the parent site using a riding model; *SHELXL96* defaults, C—H 0.93 to 0.97 Å. The isotropic factors, U_{iso} , were adjusted to 50% higher value of the parent site (methyl) and 20% higher (others). A final verification of possible voids was performed using the VOID routine of the *PLATON* program (Spek, 1995).

Data collection: CAD-4 software (Enraf–Nonius, 1989). Cell refinement: CAD-4 software (Enraf–Nonius, 1989). Data reduction: NRC-2, NRC-2A (Ahmed *et al.* 1973). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: *SHELXL96* (Sheldrick, 1996).

Supplementary data

The tables of data shown below are not normally printed in *Acta Cryst. Section C* but the data will be available electronically *via* the online contents pages at

<http://journals.iucr.org/c/journalhomepage.html>

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N1	0.1173 (2)	0.6483 (3)	0.10895 (15)	0.0377 (9)
C2	0.1579 (3)	0.6248 (4)	0.05376 (19)	0.0370 (11)
C3	0.0967 (3)	0.6425 (4)	0.0040 (2)	0.0426 (12)
C4	0.0024 (3)	0.6753 (4)	0.02591 (19)	0.0480 (13)
H4A	−0.0417	0.6080	0.0166	0.058
H4B	−0.0203	0.7523	0.0061	0.058
C5	0.0181 (3)	0.6926 (4)	0.09798 (19)	0.0373 (11)
H5	−0.0240	0.6367	0.1203	0.045
C11	0.1540 (3)	0.6294 (4)	0.17228 (19)	0.0353 (11)
C12	0.1169 (3)	0.5349 (4)	0.2079 (2)	0.0450 (13)
H12	0.0690	0.4851	0.1908	0.054
C13	0.1507 (3)	0.5136 (5)	0.2697 (2)	0.0553 (14)
H13	1/8	0.4510	0.2947	0.066
C14	0.2242 (3)	0.5898 (5)	0.2929 (2)	0.0536 (15)
H14	0.2502	0.5749	0.3332	0.064
C15	0.2583 (3)	0.6857 (5)	0.2571 (2)	0.0494 (13)
H15	0.3052	0.7372	0.2742	0.059
C16	0.2246 (3)	0.7073 (4)	0.1966 (2)	0.0447 (13)
H16	0.2482	0.7723	0.1724	0.054
C21	0.2583 (3)	0.5812 (4)	0.0537 (2)	0.0412 (12)
H21A	0.2870	0.5947	0.0954	0.049
H21B	0.2918	0.6315	0.0236	0.049
C22	0.2667 (3)	0.4417 (4)	0.0361 (2)	0.0547 (14)
H22A	0.2388	0.4291	−0.0060	0.066
H22B	0.3322	0.4202	0.0344	0.066
C23	0.2208 (3)	0.3530 (4)	0.0816 (2)	0.0622 (15)
H23A	0.1548	0.3670	0.0800	0.093
H23B	0.2451	0.3683	0.1238	0.093
H23C	0.2335	0.2675	0.0699	0.093
N31	0.1118 (3)	0.6285 (4)	−0.05986 (19)	0.0561 (12)
O31	0.0436 (2)	0.6351 (4)	−0.09787 (14)	0.0731 (12)
O32	0.1939 (3)	0.6068 (3)	−0.07733 (14)	0.0692 (12)
C51	0.0071 (3)	0.8226 (4)	0.1211 (2)	0.0392 (12)
C52	−0.0545 (3)	0.8483 (5)	0.1681 (2)	0.0518 (14)
H52	−0.0854	0.7825	0.1874	0.062
C53	−0.0703 (4)	0.9691 (6)	0.1864 (3)	0.0710 (18)
H53	−0.1128	0.9843	0.2178	0.085
C54	−0.0252 (4)	1.0693 (6)	0.1597 (3)	0.0732 (18)
H54	−0.0370	1.1515	0.1723	0.088
C55	0.0381 (4)	1.0440 (5)	0.1135 (3)	0.0697 (17)
H55	0.0702	1.1096	0.0949	0.084
C56	0.0534 (3)	0.9226 (5)	0.0954 (2)	0.0601 (15)
H56	0.0967	0.9069	0.0647	0.072

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

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
N1	0.036 (2)	0.047 (3)	0.0304 (19)	0.006 (2)	0.0054 (17)	0.0032 (19)
C2	0.047 (3)	0.029 (3)	0.035 (2)	−0.001 (2)	0.002 (2)	0.000 (2)
C3	0.049 (3)	0.045 (3)	0.034 (3)	0.000 (3)	−0.001 (2)	−0.004 (2)
C4	0.035 (3)	0.055 (3)	0.053 (3)	0.008 (3)	−0.003 (2)	−0.001 (3)

C5	0.026 (2)	0.041 (3)	0.046 (3)	0.003 (2)	0.008 (2)	0.007 (2)
C11	0.037 (3)	0.036 (3)	0.034 (2)	0.008 (2)	0.012 (2)	0.004 (2)
C12	0.032 (3)	0.054 (3)	0.050 (3)	0.000 (3)	0.007 (2)	0.004 (3)
C13	0.065 (4)	0.057 (4)	0.045 (3)	0.016 (3)	0.020 (3)	0.016 (3)
C14	0.054 (4)	0.070 (4)	0.036 (3)	0.023 (3)	0.000 (3)	-0.002 (3)
C15	0.042 (3)	0.064 (4)	0.042 (3)	0.003 (3)	0.003 (2)	-0.007 (3)
C16	0.046 (3)	0.044 (3)	0.044 (3)	-0.006 (3)	0.014 (2)	-0.004 (3)
C21	0.035 (3)	0.048 (3)	0.041 (3)	0.003 (2)	0.007 (2)	-0.001 (2)
C22	0.051 (3)	0.054 (4)	0.059 (3)	0.016 (3)	0.007 (3)	-0.005 (3)
C23	0.070 (4)	0.043 (3)	0.073 (4)	0.007 (3)	-0.001 (3)	0.001 (3)
N31	0.074 (3)	0.050 (3)	0.045 (3)	-0.004 (3)	0.002 (2)	0.003 (2)
O31	0.082 (3)	0.094 (3)	0.042 (2)	0.005 (3)	-0.0174 (19)	-0.002 (2)
O32	0.075 (3)	0.090 (3)	0.043 (2)	0.003 (2)	0.0163 (19)	0.002 (2)
C51	0.033 (3)	0.039 (3)	0.045 (3)	0.005 (2)	-0.001 (2)	-0.003 (2)
C52	0.042 (3)	0.055 (4)	0.059 (3)	-0.001 (3)	0.013 (2)	-0.011 (3)
C53	0.049 (4)	0.086 (5)	0.079 (4)	0.016 (4)	0.013 (3)	-0.018 (4)
C54	0.073 (5)	0.057 (4)	0.089 (5)	0.021 (4)	-0.017 (4)	-0.025 (4)
C55	0.071 (4)	0.054 (4)	0.084 (5)	-0.011 (3)	0.003 (3)	0.009 (4)
C56	0.064 (4)	0.037 (3)	0.081 (4)	0.003 (3)	0.025 (3)	0.003 (3)

Table S3. Geometric parameters ($\text{\AA}$, $^\circ$)

N1—C2	1.345 (4)	C21—C22	1.533 (5)
N1—C11	1.434 (5)	C21—H21A	0.9700
N1—C5	1.511 (5)	C21—H21B	0.9700
C2—C3	1.359 (5)	C22—C23	1.513 (5)
C2—C21	1.514 (5)	C22—H22A	0.9700
C3—N31	1.382 (5)	C22—H22B	0.9700
C3—C4	1.488 (5)	C23—H23A	0.9600
C4—C5	1.542 (5)	C23—H23B	0.9600
C4—H4A	0.9700	C23—H23C	0.9600
C4—H4B	0.9700	N31—O31	1.246 (4)
C5—C51	1.474 (6)	N31—O32	1.269 (4)
C5—H5	0.9800	C51—C56	1.375 (6)
C11—C12	1.373 (5)	C51—C52	1.380 (5)
C11—C16	1.393 (5)	C52—C53	1.361 (6)
C12—C13	1.395 (6)	C52—H52	0.9300
C12—H12	0.9300	C53—C54	1.378 (7)
C13—C14	1.405 (6)	C53—H53	0.9300
C13—H13	0.9300	C54—C55	1.384 (6)
C14—C15	1.369 (6)	C54—H54	0.9300
C14—H14	0.9300	C55—C56	1.365 (6)
C15—C16	1.370 (6)	C55—H55	0.9300
C15—H15	0.9300	C56—H56	0.9300
C16—H16	0.9300		

C2—N1—C11	128.8 (4)	C2—C21—C22	112.3 (4)
C2—N1—C5	111.1 (3)	C2—C21—H21A	109.2
C11—N1—C5	120.0 (3)	C22—C21—H21A	109.2
N1—C2—C3	110.9 (4)	C2—C21—H21B	109.2
N1—C2—C21	120.0 (4)	C22—C21—H21B	109.2
C3—C2—C21	129.1 (4)	H21A—C21—H21B	107.9
C2—C3—N31	128.3 (4)	C23—C22—C21	114.1 (4)
C2—C3—C4	111.3 (4)	C23—C22—H22A	108.7
N31—C3—C4	120.4 (4)	C21—C22—H22A	108.7
C3—C4—C5	103.4 (3)	C23—C22—H22B	108.7
C3—C4—H4A	111.1	C21—C22—H22B	108.7
C5—C4—H4A	111.1	H22A—C22—H22B	107.6
C3—C4—H4B	111.1	C22—C23—H23A	109.5
C5—C4—H4B	111.1	C22—C23—H23B	109.5
H4A—C4—H4B	109.0	H23A—C23—H23B	109.5
C51—C5—N1	110.6 (4)	C22—C23—H23C	109.5
C51—C5—C4	115.2 (4)	H23A—C23—H23C	109.5
N1—C5—C4	102.6 (3)	H23B—C23—H23C	109.5
C51—C5—H5	109.4	O31—N31—O32	122.7 (4)
N1—C5—H5	109.4	O31—N31—C3	118.4 (4)
C4—C5—H5	109.4	O32—N31—C3	118.9 (4)
C12—C11—C16	121.6 (4)	C56—C51—C52	117.6 (5)
C12—C11—N1	118.5 (4)	C56—C51—C5	122.2 (4)
C16—C11—N1	119.9 (4)	C52—C51—C5	120.2 (4)
C11—C12—C13	120.2 (5)	C53—C52—C51	120.6 (5)
C11—C12—H12	119.9	C53—C52—H52	119.7
C13—C12—H12	119.9	C51—C52—H52	119.7
C12—C13—C14	117.7 (5)	C52—C53—C54	121.8 (5)
C12—C13—H13	121.1	C52—C53—H53	119.1
C14—C13—H13	121.1	C54—C53—H53	119.1
C15—C14—C13	121.0 (5)	C53—C54—C55	118.0 (5)
C15—C14—H14	119.5	C53—C54—H54	121.0
C13—C14—H14	119.5	C55—C54—H54	121.0
C14—C15—C16	121.2 (5)	C56—C55—C54	119.8 (5)
C14—C15—H15	119.4	C56—C55—H55	120.1
C16—C15—H15	119.4	C54—C55—H55	120.1
C15—C16—C11	118.3 (4)	C55—C56—C51	122.3 (5)
C15—C16—H16	120.9	C55—C56—H56	118.9
C11—C16—H16	120.9	C51—C56—H56	118.9
C11—N1—C2—C3	173.3 (4)	C13—C14—C15—C16	−2.8 (7)
C5—N1—C2—C3	−2.6 (5)	C14—C15—C16—C11	0.4 (7)
C11—N1—C2—C21	−5.1 (7)	C12—C11—C16—C15	1.5 (6)
C5—N1—C2—C21	179.0 (4)	N1—C11—C16—C15	−179.5 (4)
N1—C2—C3—N31	179.7 (5)	N1—C2—C21—C22	107.4 (5)
C21—C2—C3—N31	−2.1 (8)	C3—C2—C21—C22	−70.6 (6)
N1—C2—C3—C4	−3.2 (6)	C2—C21—C22—C23	−61.7 (5)
C21—C2—C3—C4	175.0 (4)	C2—C3—N31—O31	171.8 (5)
C2—C3—C4—C5	7.3 (5)	C4—C3—N31—O31	−5.1 (7)
N31—C3—C4—C5	−175.3 (4)	C2—C3—N31—O32	−6.7 (8)
C2—N1—C5—C51	−116.5 (4)	C4—C3—N31—O32	176.5 (4)
C11—N1—C5—C51	67.3 (5)	N1—C5—C51—C56	63.4 (5)
C2—N1—C5—C4	6.9 (5)	C4—C5—C51—C56	−52.3 (6)
C11—N1—C5—C4	−169.4 (4)	N1—C5—C51—C52	−119.6 (4)
C3—C4—C5—C51	112.2 (4)	C4—C5—C51—C52	124.7 (4)
C3—C4—C5—N1	−8.0 (5)	C56—C51—C52—C53	2.1 (7)
C2—N1—C11—C12	−109.5 (5)	C5—C51—C52—C53	−175.0 (5)
C5—N1—C11—C12	66.0 (5)	C51—C52—C53—C54	−0.9 (8)
C2—N1—C11—C16	71.5 (6)	C52—C53—C54—C55	−0.5 (8)
C5—N1—C11—C16	−113.0 (4)	C53—C54—C55—C56	0.6 (8)
C16—C11—C12—C13	−1.1 (6)	C54—C55—C56—C51	0.7 (8)
N1—C11—C12—C13	179.9 (4)	C52—C51—C56—C55	−2.1 (8)
C11—C12—C13—C14	−1.2 (7)	C5—C51—C56—C55	175.0 (5)
C12—C13—C14—C15	3.1 (7)		