Supporting Information

Palladium Catalyzed Annulation of Aryl Heterocycles with Strained Alkenes

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Experimental Procedures

General: ^1H and ^{13}C NMR spectra were recorded in CDCl_3 or C_6D_6 with chemical shifts using TMS or residual chloroform as the internal standard. Coupling constants J are given in Hz. High-resolution mass spectra were obtained at 70 eV. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Toluene for the annulation reactions was freshly distilled under nitrogen from CaH_2 prior to use. All other solvents were purified by standard techniques. Unless otherwise stated all reactions were performed under an atmosphere of nitrogen.

Substrate Synthesis:

N-Aryl Pyrroles **6a-d** were prepared by Paal-Knorr synthesis from the respective aniline, according to the procedure of Lee.¹

General Method: A solution of aniline (1 equiv.) and acetic acid (0.07 mL/mmol aniline) in DCE (1.86 mL/mmol aniline) and water (1.12 mL/mmol aniline) was heated to 80 °C. 2,5-Dimethoxytetrahydrofuran (1.05 equiv.) was then added in one portion and the heating continued at 80 °C overnight. Once cooled, the layers were separated and the aqueous layer extracted with DCM. The combined organic layers were then dried (MgSO_4), filtered, and the solvent removed *in vacuo* to yield the crude pyrrole.

1-(2-Bromo-4-methyl-phenyl)-1H-pyrrole (6a)

Synthesized according to the general procedure using 2-bromo-4-methyl-aniline (3.0g, 16.12 mmol). Purified by flash column chromatography (hexane:ethyl acetate, 18:1) to yield the title compound as a yellow oil (3.0 g, 80%); $R_f = 0.85$

(hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 7.50 (1H, s), 7.22 (1H, s, $J = 7.5$), 7.16 (1H, d, $J = 7.5$), 6.88 (2H, t, $J = 2.3$), 6.34 (2H, t, $J = 2.3$), 3.40 (1H, s); δ_{C} (75 MHz, CDCl_3) 139.4, 138.2, 134.3, 129.0, 128.2, 122.6, 119.9, 109.2, 20.9; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 2252, 1709, 1507.8, 1331.3; m/z (EI) calcd. for $\text{C}_{11}\text{H}_{10}\text{NBr}$ 234.9997: found 234.9991.

1-(2-Bromo-phenyl)-1H-pyrrole² (6b)

Synthesized according to the general procedure using 2-bromo-aniline (2.0 g, 11.63 mmol). Purified by flash column chromatography (hexane:ethyl acetate, 10:1) to yield the title compound as a colourless oil (0.64 g, 75%); $R_f = 0.75$ (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 7.69 (1H, d, $J = 7.1$), 7.40-7.32 (2H, m), 7.23 (1H, ddd, $J = 7.7, 7.3, 1.9$), 6.89 (1H, t, $J = 1.9$), 6.38 (1H, t, $J = 1.9$) data identical to those reported.²

1-(2-Bromo-4-fluoro-phenyl)-1H-pyrrole (6c)

Synthesized according to the general procedure using 2-bromo-4-fluoro-aniline (2.0 g, 10.53 mmol). Purified by flash column chromatography (hexane:ethyl acetate, 10:1) to yield the title compound as a colorless oil (2.5 g, 98%); $R_f = 0.60$ (hexane:ethyl acetate, 2:1); δ_{H} (400 MHz, CDCl_3) 7.43 (1H, dd, $J = 7.8, 2.7$), 7.32 (1H, dd, $J = 8.7, 5.5$), 7.09 (1H, ddd, $J = 7.8, 5.5, 2.7$), 6.81 (2H, t, $J = 2.3$), 6.33 (2H, t, $J = 2.3$); δ_{C} (75 MHz, CDCl_3) 163.1, 159.8, 137.2, 129.6, 123.4, 122.6, 121.1, 115.5, 109.6; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 2252, 1709, 1505; m/z (EI) calcd. for $\text{C}_{10}\text{H}_7\text{NFBBr}$ 238.9745: found 238.9740.

1-(2-Bromo-4-chloro-phenyl)-1H-pyrrole (6d)

Synthesized according to the general procedure using 2-bromo-4-chloro-aniline (2.0 g, 7.80 mmol). Purified by flash column chromatography (hexane:ethyl acetate, 10:1) to yield the title compound as a yellow oil (1.90 g, 80%); $R_f = 0.64$ (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 7.69 (1H, d, $J = 2.4$), 7.35 (1H, dd, $J = 8.4, 2.4$), 7.25 (1H, d, $J = 2.9$), 6.84 (2H, t, $J = 2.2$), 6.34 (2H, t, $J = 2.2$); δ_{C} (75 MHz, CDCl_3) 139.4, 134.0, 133.6, 129.1, 128.6, 122.4, 120.6, 109.8; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 2252, 1554, 1496, 1463; m/z (EI) calcd. for $\text{C}_{10}\text{H}_7\text{NClBr}$ 254.9450: found 254.9451.

1-(2-Bromo-4-methyl-phenyl)-1H-pyrrole-2-carbaldehyde (6e)

According to the procedure of Ewen.³ Phosphorus oxychloride (0.13 g, 0.08 mL, 0.85 mmol) was added to DMF (0.06 mL, 0.85 mmol) at -10 °C, cooled by an ice-salt bath, and the mixture stirred for 10 mins. 1-(2-Bromo-4-methyl-phenyl)-1H-pyrrole (0.2 g, 0.85 mmol) in DCE (4 mL) was then added and the solution heated at 100 °C for 3h. The reaction was cooled, then washed with conc. Na₂CO₃ (10 mL) and water (10 mL), the organic layer was then dried (MgSO₄), filtered, and the solvent removed *in vacuo*. Purification by flash column chromatography (hexane:ethyl acetate, 9:1) yielded the title compound as a white solid (0.14 g, 63%); *R_f* = 0.45 (hexane:ethyl acetate, 2:1); δ_H (400 MHz, CDCl₃) 9.48 (1H, s), 7.51 (1H, s), 7.23 (1H, d, *J* = 7.9), 7.20 (1H, d, *J* = 7.9), 7.11 (1H, dd, *J* = 3.8, 1.5), 6.94-6.92 (1H, m), 6.43 (1H, dd, *J* = 4.0, 2.7), 2.40 (3H, s); δ_C (75 MHz, CDCl₃) 178.9, 141.0, 136.2, 133.9, 133.2, 131.3, 129.0, 122.0, 121.8, 111.0, 110.9, 21.9; ν_{max}/cm⁻¹ (CHCl₃) 2252, 1710, 1669, 1501, 1415; *m/z* (EI) calcd. for C₁₂H₁₂NOBr 262.9946; found 262.9943, mp = 106-108 °C (hexane:ethyl acetate, 9:1).

1-(2-Bromo-4-methyl-phenyl)-3-methyl-1H-pyrrole (6f R = Me)

According to the procedure of Jimenez.⁴ DIBAL (7.8 mL of a 1.0 M solution in Hexane, 7.0 mmol) was added dropwise to a solution of 2-methyl-succinic acid dimethyl ester (0.50 g, 3.13 mmol) in DCM (1 mL) at -78 °C and the solution stirred for 1 h. A solution of 2-bromo-phenyl-ammonium chloride (0.65 g, 3.12 mmol) in water (10 mL) was then added dropwise and the mixture warmed to room temperature and stirred overnight. Water (10 mL) was added and the resulting solution extracted with ether (3 × 20 mL), the organic layers combined, dried (MgSO₄), filtered, and the solvent removed *in vacuo*. Purification by flash column chromatography (hexane:ethyl acetate, 20:1) yielded the title compound as a colorless oil (0.10 g, 14%); *R_f* = 0.80 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, CDCl₃) 7.49 (1H, s), 7.20-7.12 (2H, m), 6.75 (1H, t, *J* = 2.4), 6.63-6.61 (1H, m), 6.16-6.14 (1H, m), 2.37 (3H, s), 2.17 (3H, s); δ_C (75 MHz, CDCl₃) 139.0, 138.3, 134.3, 129.0, 128.0, 122.4, 120.4, 120.2, 119.5, 110.8, 20.9, 12.2; ν_{max}/cm⁻¹ (CHCl₃) 2921, 2251, 1711, 1506, 1449, 1350; *m/z* (EI) calcd. for C₁₂H₁₂NBr 249.0153; found 249.0151.

1-(2-Bromo-4-methyl-phenyl)-3-phenyl-1H-pyrrole (6f R = Ph)

According to the procedure of Jimenez.⁴ DIBAL (7.8 mL of a 1.0 M solution in Hexane, 7.0 mmol) was added dropwise to a solution of 2-phenyl-succinic acid dimethyl ester (0.69 g, 3.13 mmol) in DCM (1 mL) at -78 °C and the solution stirred for 1 h. A solution of 2-bromo-phenyl-ammonium chloride (0.65 g, 3.12 mmol) in

water (10 mL) was then added dropwise and the mixture warmed to room temperature and stirred overnight. Water (10 mL) was added and the resulting solution extracted with ether (3 × 20 mL), the organic layers combined, dried (MgSO₄), filtered, and the solvent removed *in vacuo*. Purification by flash column chromatography (hexane:ethyl acetate, 9:1) yielded the title compound as a clear oil (0.25 g, 25%); R_f = 0.76 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, CDCl₃) 7.59-7.52 (3H, m), 7.38-7.25 (4H, m), 7.22-7.14 (3H, m), 6.87 (1H, t, J = 3.1), 6.63 (1H, dd, J = 3.1, 1.6), 2.40 (3H, s); δ_C (75 MHz, CDCl₃) 139.6, 138.0, 135.7, 134.4, 129.5, 129.2, 128.9, 128.1, 125.9, 125.43, 123.6, 119.6, 119.2, 107.6, 21.0; ν_{max}/cm^{-1} (CHCl₃) 2251, 1716, 1605, 1558, 1507; m/z (EI) calcd. for C₁₇H₁₄NBr 311.0310: found 311.0305.

1-(2-Bromo-4-methyl-phenyl)-3-phenyl-1H-pyrrole-2-carbaldehyde (6g)

According to the procedure of Ewen.³ Phosphorus oxychloride (0.21 g, 0.13 mL, 1.42 mmol) was added to DMF (0.11 mL, 1.42 mmol) at -10 °C, cooled by an ice-salt bath, and the mixture stirred for 10 mins. 1-(2-Bromo-4-methyl-phenyl)-3-phenyl-1H-pyrrole (0.44 g, 1.42 mmol) in DCE (10 mL) was then added and the solution heated at 100 °C for 3h. The reaction was cooled, then washed with conc. Na₂(CO₃)₂ (20 mL) and water (20 mL), the organic layer

was then dried (MgSO₄), filtered, and the solvent removed *in vacuo*. Purification by flash column chromatography (hexane:ethyl acetate, 10:1) yielded the title compound as a white solid (0.28 g, 60%); R_f = 0.55 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, CDCl₃) 9.64 (1H, s), 7.56-7.50 (3H, m), 7.48-7.48 (3H, m), 7.28-7.20 (2H, m), 6.92 (1H, d, J = 2.4), 6.51 (1H, d, J = 2.4); δ_C (75 MHz, CDCl₃) 178.7, 140.8, 136.4, 133.9, 130.0, 130.0, 129.4, 129.1, 129.0, 128.9, 121.9, 112.7, 112.7, 21.2; ν_{max}/cm^{-1} (CHCl₃) 2252, 1662, 1504, 1435, 1389; m/z (EI) calcd. for C₁₈H₁₄NOBr 339.0259: found 339.0261, mp = 109-111 °C (hexane:ethyl acetate, 10:1).

4-(2-Bromo-phenyl)-1H-pyrrole-3-carboxylic acid ethyl ester

According to the procedure of Lindsey.⁵ A solution of 3-(2-bromophenyl)-acrylic acid ethyl ester (3.15 g, 12.35 mmol) and TOSMIC (2.4 g, 12.35 mmol) in ether (25 mL) was added to a suspension of sodium hydride (0.6 g of a 60% suspension in mineral oil, 14.82 mmol) in a 2:1 solution of ether and DMF (60 mL) dropwise over 30 mins at room temperature. The

reaction was then stirred for 3 h before being quenched with water (50 mL) and the resulting solution extracted with ether (3 × 50 mL). The combined organic layers were then dried (MgSO₄), filtered, and the solvent removed *in vacuo*. Purification by flash column chromatography (hexane:ethyl acetate, 4:1) yielded the title compound as a yellow solid (2.39 g, 66%); R_f = 0.25 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, CDCl₃) 8.60-8.40 (1H, brs), 7.60 (1H,

d, $J = 8.2$), 7.51 (1H, t, $J = 2.9$), 7.32-7.25 (2H, m), 7.16 (1H, ddd, $J = 7.6, 7.4, 2.9$), 6.75 (1H, t, $J = 2.3$), 4.14 (2H, q, $J = 7.0$), 1.10 (3H, t, $J = 7.0$); δ_{C} (75 MHz, CDCl_3) 164.9, 136.6, 132.4, 132.1, 128.6, 126.8, 125.4, 125.4, 125.3, 124.3, 118.9, 115.7, 59.8, 14.2; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 2252, 1700, 1469, 1375; m/z (EI) calcd. for $\text{C}_{13}\text{H}_{12}\text{NO}_2\text{Br}$ 293.0051; found 293.0046, mp = 141-143 °C (hexane:ethyl acetate, 4:1).

3-(2-Bromo-phenyl)-1H-pyrrole⁶

According to the procedure of Lindsey.⁷ Powdered NaOH (0.85g, 21.1 mmol) was added to a stirred solution of 4-(2-bromo-phenyl)-1H-pyrrole-3-carboxylic acid ethyl ester (2.39 g, 8.13 mmol) in ethylene glycol (22 mL). The mixture was placed in a pre-heated oil bath at 120 °C the temperature raised to 160 °C and stirring continued at this temperature for 2.5 h. The reaction was cooled, 10% NaCl solution (100 mL) was added and the reaction extracted with DCM (3 × 60 mL). The combined organic layers were then dried (MgSO_4), filtered, and the solvent removed *in vacuo*. The resulting oil was purified by flash column chromatography (hexane:ethyl acetate, 9:1) to yield the title compound as a yellow oil (1.32 g, 73%); $R_f = 0.40$ (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 8.40-8.20 (1H, brs), 7.62 (1H, d, $J = 8.8$), 7.44 (1H, d, $J = 8.1$), 7.29 (1H, t, $J = 8.8$), 7.20-7.16 (1H, m), 7.07 (1H, t, $J = 8.1$), 6.85 (1H, s), 6.54 (1H, s); data identical to those reported.⁶

3-(2-Bromo-phenyl)-1-methyl-1H-pyrrole (6i)

3-(2-Bromo-phenyl)-1H-pyrrole (0.5 g, 2.25 mmol) in DMF (2 mL) was added dropwise to sodium hydride (90.0 mg, of a 60% suspension in mineral oil, 2.25 mmol) suspended in DMF (8 mL) and the reaction stirred at room temperature for 1 h. Iodomethane (0.32 g, 2.25 mmol) in DMF (5 mL) was then added dropwise and the reaction stirred at room temperature for 2 h. The reaction was quenched with water (20 mL) and the resulting solution extracted with ether (3 × 20 mL). The combined organic layers were then dried (MgSO_4), filtered, and the solvent removed *in vacuo*. Purification by flash column chromatography (hexane:ethyl acetate, 20:1) yielded the title compound as a colorless oil (0.40 g, 75%); $R_f = 0.50$ (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 7.60 (1H, d, $J = 8.3$), 7.41 (1H, dd, $J = 7.6, 1.1$), 7.26 (1H, td, $J = 7.6, 0.9$), 7.03 (1H, td, $J = 8.3, 0.9$), 7.00 (1H, t, $J = 1.1$), 6.63 (1H, t, $J = 2.3$), 6.44 (1H, dd, $J = 2.3, 1.5$), 3.71 (3H, s); δ_{C} (75 MHz, CDCl_3) 137.1, 133.7, 130.9, 127.4, 127.1, 123.5, 122.2, 121.7, 121.7, 109.7, 77.6, 77.2, 76.8, 36.5; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 2252, 1588, 1554, 1503, 1471; m/z (EI) calcd. for $\text{C}_{11}\text{H}_{10}\text{NBr}$ 234.9997; found 234.9999.

4-(2-Bromo-phenyl)-1-methyl-1H-pyrrole-3-carboxylic acid ethyl ester (6h)

4-(2-Bromo-phenyl)-1H-pyrrole-3-carboxylic acid ethyl ester (0.5 g, 1.70 mmol) in DMF (2 mL) was added dropwise to sodium hydride (68.0 mg, of a 60% suspension in mineral oil, 1.70 mmol) suspended in DMF (8 mL) and the reaction stirred at room temperature for 1 h. Iodomethane (0.24 g, 1.70 mmol) in DMF (5 mL) was then added dropwise and the reaction stirred at room temperature for 2 h. The reaction was quenched with water (20 mL) and the resulting solution extracted with ether (3×20 mL). The combined organic layers were then dried (MgSO_4), filtered, and the solvent removed *in vacuo*. Purification by flash column chromatography (hexane:ethyl acetate, 4:1) yielded the title compound as a yellow oil (0.64 g, 88%); $R_f = 0.40$ (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 7.60 (1H, d, $J = 7.5$), 7.32-7.25 (3H, m), 7.13 (1H, ddd, $J = 7.5, 7.3, 3.0$), 6.55 (1H, d, $J = 2.4$), 4.10 (2H, q, $J = 7.0$), 3.71 (3H, s), 1.10 (3H, t, $J = 7.0$); δ_{C} (100 MHz, CDCl_3) 164.2, 136.6, 132.1, 131.9, 128.2, 127.3, 126.5, 125.5, 125.1, 122.4, 59.4, 36.6, 14.0; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 2252, 1695, 1537, 1470; m/z (EI) calcd. for $\text{C}_{14}\text{H}_{14}\text{NO}_2\text{Br}$ 307.0208: found 307.0204, mp = 104-106 °C (hexane:ethyl acetate, 4:1).

1-(2-Bromo-phenyl)-1H-indole (4j)

According to the procedure of Ma.⁸ A flask was charged with copper(I) iodide (81.9 mg, 0.43 mmol), *N,N'*-dimethyl-ethane-1,2-diamine (0.15 g, 1.71 mmol), and K_3PO_4 (3.81 g, 17.9 mmol) the flask was then purged with argon. Toluene (10 mL) was added followed by indole (1.0 g, 8.54 mmol) and 1,2-dibromo-benzene (2.11 g, 8.96 mmol). The mixture was then heated at reflux for 24 h. Once cooled, the reaction was quenched with water (20 ml) and extracted with ether (3×20 ml). The combined organic layers were then dried (MgSO_4), filtered, and the solvent removed *in vacuo*. Purification by flash column chromatography (hexane:ethyl acetate, 20:1) yielded the title compound as a colorless oil (0.5 g, 22%); $R_f = 0.50$ (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 7.77 (1H, d, $J = 6.8$), 7.70 (1H, dd, $J = 8.3, 3.1$), 7.47-7.44 (2H, m), 7.36-7.30 (1H, m), 7.24 (1H, d, $J = 3.6$), 7.21-7.16 (2H, m), 7.12-7.08 (1H, m), 6.70 (1H, d, $J = 3.6$); δ_{C} (75 MHz, CDCl_3) 136.7, 133.9, 129.7, 129.5, 128.7, 128.3, 122.2, 121.9, 120.9, 120.3, 110.6, 103.0; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 2252, 1587, 1513, 1486, 1456, 1331; m/z (EI) calcd. for $\text{C}_{14}\text{H}_{10}\text{NBr}$ 270.9997: found 270.9996.

Annulation Reactions:

General Procedure: A sealable tube was charged with the substrate (1 equiv., 0.2 mmol), palladium(II) acetate (0.1 equiv.), triphenylphosphine (0.22 equiv.), Cs₂CO₃ (1 equiv.), and the strained alkene to be annulated (3/4 equiv. see experimental). Toluene (1 mL) was added and the tube flushed with nitrogen and sealed. The reaction was then heated at the appropriate temperature (see experimental) overnight. Once cooled, the reaction was diluted with DCM, then filtered through CeliteTM, washing with DCM. The solvent was removed *in vacuo* to provide the crude products.

Note: The reactions were carried out in sealable tubes for convenience and due to the lower boiling points of some of the strained alkenes. The reactions behave similarly at reflux under nitrogen, an extra equivalent of the strained alkene may be required under these conditions to ensure complete conversion.

Annulation Product 5

Synthesized from 2-bromo-biphenyl and norbornadiene (3 equiv.) at 130 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (49.2 mg, 100%); R_f = 0.80 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, CDCl₃) 7.75-7.69 (2H, m), 7.49-7.41 (3H, m), 7.35-7.24 (2H, m), 7.03 (1H, d, J = 7.1), 6.26-6.24 (2H, s), 3.38 (1H, d, J = 4.2), 3.18 (1H, d, J = 4.2), 2.88-2.85 (1H, m), 2.84-2.81 (1H, m), 1.30 (1H, d, J = 9.6), 0.97 (1H, d, J = 9.6); δ_C (75 MHz, CDCl₃) 147.1, 143.2, 138.5, 137.1, 136.8, 134.8, 129.0, 128.5, 127.5, 127.2, 125.0, 121.0, 48.8, 47.5, 41.9, 41.8, 41.6; ν_{max}/cm^{-1} (CHCl₃) 3064, 2972, 2251, 1595, 1464, 1321; m/z (EI) calcd. for C₁₉H₁₆ 244.1252; found 244.1259.

Annulation Product 7a

Synthesized from 1-(2-bromo-4-methyl-phenyl)-1H-pyrrole **6a** and norbornene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a white solid (50.5 mg, 100%); R_f = 0.50 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, CDCl₃) 7.21 (1H, d, J = 8.2), 7.11-7.08 (1H, m), 7.05 (1H, s), 6.94 (1H, d, J = 8.2), 6.26 (1H, t, J = 3.5), 5.79-5.77 (1H, m), 3.20 (1H, d, J = 10.0), 3.00 (1H, d, J = 10.0), 2.41 (1H, s), 2.37 (1H, s), 2.29 (3H, s), 1.66-1.63 (2H, m), 1.54-1.50 (2H, m), 1.27 (1H, d, J = 10.1), 1.05 (1H, d, J = 10.1); δ_C (75 MHz, CDCl₃) 133.2, 132.5, 131.2, 128.3, 127.6, 122.5,

113.9, 112.8, 110.5, 106.7, 48.7, 48.2, 43.7, 40.7, 34.4, 30.1, 29.0, 21.0; $\nu_{\max}/\text{cm}^{-1}$ (CHCl_3) 2975, 1934, 1861, 1964, 1443, 1381, 1350; m/z (EI) calcd. for $\text{C}_{18}\text{H}_{19}\text{N}$ 249.1518: found 249.1520, mp = 112-114 °C (hexane:ethyl acetate, 20:1).

Annulation Product 7b

Synthesized from 1-(2-bromo-phenyl)-1H-pyrrole **6b** and norbornene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (39.0 mg, 83%); R_f = 0.80 (hexane:ethyl acetate, 2:1); δ_{H} (400 MHz, C_6D_6) 6.68-6.62 (2H, m), 6.58-6.45 (3H, m), 6.03 (1H, t, J = 3.6), 5.71-5.69 (1H, m), 2.61 (1H, d, J = 9.6), 2.28 (1H, d, J = 9.6), 1.93 (1H, s), 1.73 (1H, s), 1.00, 0.78 (5H, m), 0.41 (1H, d, J = 9.8); δ_{C} (75 MHz, C_6D_6) 130.9, 130.6, 126.9, 123.6, 122.1, 113.9, 113.0, 111.3, 109.8, 107.5, 48.6, 48.2, 43.6, 40.7, 34.1, 29.9, 28.7; $\nu_{\max}/\text{cm}^{-1}$ (CHCl_3) 2956, 2870, 2251, 1699, 1591, 1503, 1470; m/z (EI) calcd. for $\text{C}_{17}\text{H}_{18}\text{N}$ 236.1443: found 236.1445.

Annulation Product 7c

Synthesized from 1-(2-bromo-4-fluoro-phenyl)-1H-pyrrole **6c** and norbornene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (40.9 mg, 81%); R_f = 0.75 (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, C_6D_6) 6.45 (1H, dd, J = 3.0, 2.1), 6.36 (1H, dd, J = 8.9, 4.9), 6.28-6.14 (2H, m), 5.99 (1H, t, J = 3.3), 5.67-5.64 (1H, m), 2.51 (1H, d, J = 9.3), 2.09 (1H, d, J = 9.3), 1.88 (1H, s), 1.55 (1H, s), 1.00-0.64 (5H, m), 0.36 (1H, d, J = 10.3); δ_{C} (75 MHz, C_6D_6) 160.9, 157.8, 131.3, 130.5, 116.9, 116.5, 115.1, 113.4, 113.0, 111.3, 107.5, 48.4, 48.2, 43.7, 40.6, 34.0, 29.7, 28.6; $\nu_{\max}/\text{cm}^{-1}$ (CHCl_3) 2948, 2252, 1709, 1511; m/z (EI) calcd. for $\text{C}_{17}\text{H}_{16}\text{NF}$ 253.1267: found 253.1269.

Annulation Product 7d

Synthesized from 1-(2-bromo-4-chloro-phenyl)-1H-pyrrole **6d** and norbornene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a white solid (48.0 mg, 89%); R_f = 0.62 (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 7.25-7.20 (1H, m), 7.09 (1H, dd, J = 8.2, 2.1), 7.05 (1H, dd, J = 2.1, 1.7), 6.28 (1H, t, J = 3.4), 6.02-5.98 (1H, m), 3.20 (1H, d, J = 9.5), 2.98 (1H, d, J = 9.5), 2.41 (1H, s), 2.36 (1H, s), 1.70-1.48 (4H, m), 1.25 (1H, d, J = 10.6), 1.08 (1H, d, J = 10.6); δ_{C}

(75 MHz, CDCl₃) 133.5, 131.2, 130.4, 128.8, 127.0, 126.9, 115.4, 113.1, 111.3, 107.4, 48.7, 48.2, 43.7, 40.7, 34.4, 29.9, 28.9; $\nu_{\max}/\text{cm}^{-1}$ (CHCl₃) 2956, 2866, 2252, 1502, 1334; m/z (EI) calcd. for C₁₇H₁₆NCl 269.0971: found 269.0970, mp = 114-116 °C (hexane:ethyl acetate, 20:1).

Annulation Product 7e

Synthesized from 1-(2-bromo-4-methyl-phenyl)-1H-pyrrole-2-carbaldehyde **6e** and norbornene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (49.1 mg, 89%); R_f = 0.50 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, CDCl₃) 9.52 (1H, s), 8.09 (1H, d, J = 8.8), 7.15 (1H, dd, J = 4.2), 7.03 (1H, s), 7.01 (1H, d, J = 8.8), 6.17 (1H, d, J = 4.2), 3.27 (1H, d, J = 10.0), 3.01 (1H, d, J = 10.0), 2.43 (2H, s), 2.31 (3H, s), 1.72-1.66 (2H, m), 1.60-1.52 (2H, m), 1.30 (1H, d, J = 10.5), 1.11 (1H, d, J = 10.5); δ_C (75 MHz, CDCl₃) 177.3, 145.2, 135.4, 131.8, 131.7, 131.6, 130.7, 128.9, 127.8, 120.2, 109.4, 48.5, 48.3, 43.8, 41.9, 34.6, 30.3, 28.9, 20.9; $\nu_{\max}/\text{cm}^{-1}$ (CHCl₃) 2958, 2873, 2252, 1710, 1657, 1506, 1474, 1419; m/z (EI) calcd. for C₁₉H₁₉NO 277.1467: found 277.1460.

Annulation Products 7f and 7g (R = Me)

Synthesized from 1-(2-bromo-4-methyl-phenyl)-3-methyl-1H-pyrrole **6f** and norbornene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compounds as an inseparable mixture and as a colorless oil (50.0 mg, 95%, 1.47:1 ratio); R_f = 0.70 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, CDCl₃) 7.22-6.84, (8H, m, 4H major and 4H minor), 6.10 (1H, d, J = 2.9, major), 5.83 (1H, s, minor), 3.17-2.95 (4H, m, 2H major and 2H minor), 2.40-2.36 (4H, m, 2H major and 2H minor), 2.28 (6H, s, 3H major and 3H minor), 2.12 (3H, s, minor), 2.07 (3H, s, major), 1.70-1.50 (10H, m, 5H major and 5H minor), 1.34-1.28 (2H, m, 1H major and 1H, minor), 1.08-1.02 (2H, m, 1H major and 1H, minor); δ_C (75 MHz, CDCl₃) 132.8, 132.7, 132.6, 132.5, 131.1, 131.1, 130.9, 130.2, 129.7, 128.1, 128.1, 127.9, 127.5, 127.5, 126.5, 121.3, 120.2, 115.5, 113.6, 113.5, 112.2, 112.2, 112.1, 111.8, 110.8, 110.7, 108.4, 48.6, 48.3, 48.2, 45.4, 44.0, 43.6, 40.7, 39.8, 34.4, 34.2, 30.0, 29.7, 29.5, 29.0, 29.0, 21.0, 20.9, 12.4, 11.7; $\nu_{\max}/\text{cm}^{-1}$ (CHCl₃) 2956, 2870, 2251, 1711, 1601, 1514, 1450, 1367; m/z (EI) calcd. for C₁₉H₂₁N 263.1675: found 263.1672.

Annulation Products 7f and 7g (R = Phenyl)

Synthesized from 1-(2-bromo-4-methyl-phenyl)-3-phenyl-1H-pyrrole **6f** and norbornene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compounds as an inseparable mixture and as a colorless oil (54.5 mg, 84%, 1.67:1 ratio); R_f = 0.65 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, $CDCl_3$)

7.58-7.50 (4H, m, 2H major and 2H minor), 7.40-7.18 (), 7.07 (2H, s, 1H major and 1H minor), 7.00-7.95 (2H, m, 1H, major and 1H minor), 6.50 (1H, d, J = 2.9, major), 6.32 (1H, s, minor), 3.61 (1H, d, J = 10.2, major), 3.22 (1H, d, J = 10.1, minor), 3.09 (1H, d, J = 10.2, major), 3.00 (1H, d, J = 10.1, minor), 2.47 (1H, s, minor), 2.39 (2H, s, 1H major and 1H minor), 2.30 (6H, s, 3H major and 3H minor), 2.23 (1H, s), 1.72-0.80 (12H, m, 6H major and 6H minor); δ_C (75 MHz, $CDCl_3$) 137.1, 135.6, 133.4, 132.5, 132.3, 132.2, 131.2, 130.9, 129.8, 128.9, 128.8, 128.8, 128.7, 128.6, 128.2, 127.7, 127.6, 127.4, 126.6, 126.6, 125.9, 125.4, 125.4, 125.2, 125.1, 121.5, 120.5, 114.0, 113.8, 113.6, 111.1, 109.3, 105.2, 48.6, 48.6, 48.3, 45.9, 44.1, 43.6, 40.7, 40.4, 34.5, 34.4, 30.1, 29.7, 29.5, 29.0, 28.8, 21.0; ν_{max}/cm^{-1} ($CHCl_3$) 2956, 2871, 2252, 1708, 1515, 1393, 1356; m/z (EI) calcd. for $C_{24}H_{23}N$ 325.1831: found 325.1835.

Annulation Product 7h

Synthesized from 1-(2-bromo-4-methyl-phenyl)-3-phenyl-1H-pyrrole-2-carbaldehyde **6g** (0.1 mmol) and norbornene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 10:1) yielding the title compound as a colorless oil (31.8 mg, 90%); R_f = 0.70 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, $CDCl_3$) 9.48 (1H, s), 7.84 (1H, d, J = 8.8), 7.55-7.38 (5H, m), 7.03 (1H, s),

7.02 (1H, d, J = 8.8), 6.25 (1H, s), 3.30 (1H, d, J = 9.9), 3.04 (1H, d, J = 9.9), 2.48 (2H, s), 2.31 (3H, s), 1.76-1.12 (4H, m), 0.90-0.80 (2H, m); δ_C (75 MHz, $CDCl_3$) 179.2, 146.5, 144.3, 135.1, 133.9, 131.4, 130.2, 129.8, 128.5, 128.3, 128.1, 127.2, 126.7, 120.6, 109.8, 48.1, 48.0, 43.8, 41.6, 34.5, 30.2, 28.6, 20.7; ν_{max}/cm^{-1} ($CHCl_3$) 2958, 2871, 2251, 1647, 1506, 1456, 1398; m/z (EI) calcd. for $C_{25}H_{24}NO$ 354.1852: found 384.1861.

Annulation Product 6i

Synthesized from 4-(2-bromo-phenyl)-1-methyl-1H-pyrrole-3-carboxylic acid ethyl ester **6h** and norbornene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography

(hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (59.0 mg, 92%); R_f = 0.40 (hexane:ethyl acetate, 10:1); δ_H (300 MHz, $CDCl_3$) 8.72 (1H, d, J = 7.7), 7.27 (1H, s), 7.15-7.00 (3H, m), 4.32-4.24 (2H, m), 3.51 (3H, s), 3.28 (1H, d, J = 10.2), 3.95 (1H, d, J = 10.2), 2.41 (1H, s), 2.24 (1H, s), 1.78-1.46 (5H, m), 1.36 (3H, t, J = 6.9), 1.09 (1H, dd, J = 10.0); δ_C (75 MHz, $CDCl_3$) 165.5, 136.1, 133.0, 131.3, 130.6, 128.9, 126.3, 125.7, 125.6, 117.1, 111.4, 59.8, 48.9, 48.1, 44.9, 40.3, 34.0, 33.8, 30.0, 29.6, 14.7; ν_{max}/cm^{-1} ($CHCl_3$) 2956, 2871, 2252, 1699, 1524, 1425; m/z (EI) calcd. for $C_{21}H_{23}NO_2$ 321.1729; found 321.1736.

Annulation Product 6j

Synthesized from 3-(2-bromo-phenyl)-1-methyl-1H-pyrrole **6i** and norbornene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (51.4 mg, 85%); R_f = 0.60 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, C_6D_6) 7.03 (1H, d, J = 7.1), 6.68-6.64 (2H, m), 6.62-6.59 (1H, m), 6.05 (1H, d, J = 2.9), 5.86 (1H, d, J = 2.9), 2.71 (1H, d, J = 9.4), 2.39 (3H, s), 2.21 (1H, d, J = 9.4), 1.92 (1H, d, J = 3.6), 1.57 (1H, d, J = 3.6), 1.21 (1H, d, J = 9.8), 1.08-0.77 (4H, m), 0.48 (1H, d, J = 9.8); δ_C (75 MHz, C_6D_6) 135.4, 133.1, 129.9, 129.2, 126.5, 124.7, 122.3, 121.4, 117.8, 102.4, 48.7, 48.5, 44.4, 40.8, 33.9, 32.5, 29.9, 29.7; ν_{max}/cm^{-1} ($CHCl_3$) 2956, 2870, 2251, 1603, 1558, 1509, 1448; m/z (EI) calcd. for $C_{18}H_{19}N$ 249.1518; found 249.1518.

Annulation Product 9

Synthesized from 1-(2-bromo-4-methyl-phenyl)-1H-pyrrole **6a** and 1,4-dihydro-1,4-methano-naphthalene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (63.8 mg, 100%); R_f = 0.50 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, $CDCl_3$) 7.36-7.32 (2H, m), 7.29 (1H, d, J = 8.2), 7.23 (1H, s), 7.20-7.15 (2H, m), 7.01 (1H, d, J = 6.4), 6.33 (1H, t, J = 3.6), 6.19-6.16 (1H, m), 3.49 (1H, s), 3.45 (1H, s), 3.24 (1H, d, J = 9.3), 3.04 (1H, d, J = 9.3), 2.36 (3H, s), 1.63 (2H, s); δ_C (75 MHz, $CDCl_3$) 147.8, 147.3, 133.2, 132.5, 130.9, 130.5, 127.7, 127.2, 126.1, 121.3, 120.8, 113.9, 112.9, 110.5, 107.0, 55.6, 55.5, 44.8, 41.5, 38.0, 20.7; ν_{max}/cm^{-1} ($CHCl_3$) 2976, 2251, 1708, 1515, 1468, 1336; m/z (EI) calcd. for $C_{22}H_{19}N$ 297.1518; found 297.1525.

Annulation Product 11

Synthesized from 1-(2-bromo-4-methyl-phenyl)-1H-pyrrole **6a** and 11-Oxa-tricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a white solid (46.9 mg, 79%); R_f = 0.72 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, C_6D_6) 7.04-6.96 (4H, m), 6.90-6.86 (2H, m), 6.76-6.70 (2H, m), 6.42 (1H, d, J = 3.6), 6.19-6.16 (1H, m), 5.34 (1H, s), 5.19 (1H, s), 3.20 (1H, d, J = 9.3), 2.85 (1H, d, J = 9.3), 2.10 (3H, s); δ_C (75 MHz, C_6D_6) 145.7, 145.5, 143.0, 132.9, 130.7, 126.9, 126.8, 125.9, 124.8, 120.1, 119.5, 119.0, 114.2, 113.7, 111.0, 107.7, 89.5, 89.3, 42.3, 38.9, 20.6; ν_{max}/cm^{-1} ($CHCl_3$) 2976, 2931, 2865, 1444, 1382, 1350; m/z (EI) calcd. for $C_{21}H_{17}NO$ 299.1310: found 293.1316; mp = 175-177 °C (hexane:ethyl acetate, 20:1).

Annulation Product 13

Synthesized from 1-(2-bromo-4-methyl-phenyl)-1H-pyrrole **6a** and 5,6-Bis-methoxymethyl-7-oxa-bicyclo[2.2.1]hept-2-ene (3 equiv.) at 110 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 6:1) yielding the title compound as a white solid (61.6 mg, 91%); R_f = 0.20 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, $CDCl_3$) 7.22 (1H, d, J = 8.2), 7.13-7.11 (1H, m), 7.07 (1H, s), 6.97 (1H, d, J = 8.2), 6.27 (1H, t, J = 3.0), 6.10-6.07 (1H, m), 4.46 (1H, s), 4.45 (1H, s), 3.52 (1H, d, J = 9.6), 3.44-3.24 (3H, m), 3.37 (3H, s), 3.35 (3H, s), 2.45-2.40 (2H, m), 2.31 (3H, s); δ_C (75 MHz, $CDCl_3$) 133.4, 132.5, 130.7, 128.6, 128.1, 125.9, 114.1, 113.4, 110.6, 107.2, 107.2, 89.1, 89.0, 77.6, 77.2, 76.8, 71.2, 71.1, 59.1, 59.0, 59.0, 45.9, 45.1, 44.3, 41.4, 20.9; ν_{max}/cm^{-1} ($CHCl_3$) 2925, 2248, 1517, 1572, 1338; m/z (EI) calcd. for $C_{21}H_{25}NO_3$ 339.1834: found 339.1842; mp = 123-125 °C (hexane:ethyl acetate, 6:1).

Annulation Product 15a

Synthesized from 1-(2-bromo-4-methyl-phenyl)-1H-pyrrole **6a** and norbornadiene (3 equiv.) at 80 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (35.4 mg, 94%); R_f = 0.80 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, $CDCl_3$) 7.27 (1H, d, J = 8.3), 7.16-7.13 (2H, m), 6.98 (1H, d, J = 8.3), 6.35-6.29 (3H, m), 6.08-6.06 (1H, m), 3.07 (1H, d, J = 9.4), 3.02 (1H, s), 2.98 (1H, s), 2.88 (1H, d, J = 9.4), 2.33 (3H, s), 1.24 (3H, s); δ_C (75 MHz, $CDCl_3$) 137.2, 137.1, 133.0, 132.5,

131.4, 130.9, 127.8, 127.4, 113.7, 112.7, 110.3, 106.5, 54.1, 53.9, 44.0, 39.3, 35.6, 20.7; $\nu_{\max}/\text{cm}^{-1}$ (CHCl_3) 2975, 2932, 2860, 1963, 1444, 1381, 1350; mp = 80-82 °C (hexane:ethyl acetate, 20:1).

Note: HRMS cannot be measured as compound decomposes under mass. spec. conditions showing a peak under E.I. at m/z 181.0875, corresponding to **16a** the retro Diels-Alder Product.

Annulation Product 16a

Synthesized from 1-(2-bromo-4-methyl-phenyl)-1H-pyrrole **6a** and norbornadiene (4 equiv.) at 120 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (46.5 mg, 98%); R_f = 0.71 (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 7.79 (1H, s), 7.75 (1H, d, J = 7.9), 7.41 (1H, s), 7.31-7.24 (2H, m), 6.91 (1H, d, J = 8.7), 6.75 (1H, t, J = 2.8), 6.48 (1H, d, J = 4.7), 2.44 (3H, s); δ_{C} (75 MHz, C_6D_6) 132.5, 131.8, 131.1, 128.7, 128.6, 124.0, 119.2, 118.4, 114.1, 112.7, 112.0, 103.2, 20.7; $\nu_{\max}/\text{cm}^{-1}$ (CHCl_3) 2975, 2933, 2862, 1444, 1382, 1350; m/z (EI) calcd. for $\text{C}_{13}\text{H}_{11}\text{N}$ 181.0891: found 181.0892; mp = 70-72 °C (hexane:ethyl acetate, 20:1).

Annulation Product 16b⁹

Synthesized from 1-(2-bromo-phenyl)-1H-pyrrole **6b** and norbornadiene (4 equiv.) at 120 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (30.7 mg, 92%); R_f = 0.75 (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 7.87 (1H, d, J = 8.0), 7.83 (1H, d, J = 1.3), 7.62 (1H, d, J = 9.3), 7.49 (1H, t, J = 8.8), 7.32-7.28 (2H, m), 6.97 (1H, d, J = 9.3), 6.78 (1H, t, J = 4.0), 6.52 (1H, d, J = 4.0); data identical to those reported.⁹

Annulation Product 16c

Synthesized from 1-(2-bromo-4-fluoro-phenyl)-1H-pyrrole **6c** and norbornadiene (4 equiv.) at 120 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a white solid (31.7 g, 86%); R_f = 0.70 (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, C_6D_6) 7.38 (1H, d, J = 0.5), 7.08 (1H, dd, J = 9.4, 4.7), 7.01 (1H, d, J = 9.4), 6.94 (1H, dd, J = 9.6, 2.9), 6.82 (1H, dd, J = 7.6, 2.4), 6.77 (1H, dd, J = 6.0, 2.4), 6.53 (1H, d, J = 4.2), 6.41 (1H, d, J = 9.4); δ_{C} (75 MHz, C_6D_6) 160.6, 157.4, 120.3, 117.7, 117.6, 115.8, 115.7, 115.2, 114.8,

113.5, 113.2, 112.9, 112.4, 103.7; $\nu_{\max}/\text{cm}^{-1}$ (CHCl_3) 2252, 1631, 1561, 1487, 1529, 1323; m/z (EI) calcd. for $\text{C}_{12}\text{H}_8\text{NF}$ 185.0641; found 185.0644; mp = 74-77 °C (hexane:ethyl acetate, 20:1).

Annulation Product 16d

Synthesized from 1-(2-Bromo-4-chloro-phenyl)-1H-pyrrole **6d** and norbornadiene (4 equiv.) at 120 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a white solid (37.3 mg, 93%); R_f = 0.60 (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 7.78-7.76 (2H, m), 7.57 (1H, d, J = 2.4), 7.30 (1H, dd, J = 8.7, 2.3), 7.31 (1H, d, J = 9.4), 6.86 (1H, d, J = 9.4), 6.78 (1H, t, J = 3.4), 6.53 (1H, dd, J = 3.4, 1.6); δ_{C} (75 MHz, CDCl_3) 132.1, 131.0, 129.0, 127.9, 127.8, 125.4, 120.5, 117.8, 115.8, 113.3, 112.5, 103.6; $\nu_{\max}/\text{cm}^{-1}$ (CHCl_3) 2251, 1549, 1484, 1426, 1320; m/z (EI) calcd. for $\text{C}_{12}\text{H}_8\text{NCl}$ 201.0345; found 201.0345; mp = 87-89 °C (hexane:ethyl acetate, 20:1).

Annulation Product 16e

Synthesized from 1-(2-bromo-4-methyl-phenyl)-1H-pyrrole-2-carbaldehyde **6e** and norbornadiene (4 equiv.) at 120 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 4:1) yielding the title compound as a white solid (30.1 mg, 72%); R_f = 0.40 (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 9.69 (1H, s), 9.35 (1H, d, J = 8.1), 7.51 (1H, d, J = 8.1), 7.45-7.43 (2H, m), 7.37 (1H, d, J = 9.5), 7.33 (1H, d, J = 9.5), 7.63 (1H, d, J = 4.9), 2.45 (3H, s); δ_{C} (75 MHz, CDCl_3) 176.3, 140.8, 135.1, 133.3, 132.5, 130.0, 128.1, 126.8, 125.1, 120.8, 117.9, 106.0, 21.1; $\nu_{\max}/\text{cm}^{-1}$ (CHCl_3) 2250, 1709, 1652, 1467, 1415, 1322; m/z (EI) calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}$ 209.0841; found 209.0846; mp = 77-79 °C (hexane:ethyl acetate, 4:1).

Annulation Product 16g

Synthesized from 1-(2-bromo-4-methyl-phenyl)-3-phenyl-1H-pyrrole-2-carbaldehyde **6g** (0.1 mmol scale) and norbornadiene (4 equiv.) at 120 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 8:1) yielding the title compound as a colorless oil (24.0 mg, 84%); R_f = 0.60 (hexane:ethyl acetate, 2:1); δ_{H} (300 MHz, CDCl_3) 9.63 (1H, s), 9.00 (1H, d, J = 8.8), 7.60-7.56 (2H, m), 7.52-7.16 (7H, m), 6.69 (1H, s), 2.50 (1H, s); δ_{C} (75 MHz, CDCl_3) 178.4, 146.9, 139.1, 135.1, 134.4, 132.9, 130.6, 129.8, 128.6, 128.4, 128.0, 127.8, 126.0, 125.6, 125.3, 121.3, 117.5, 106.5, 21.2; $\nu_{\max}/\text{cm}^{-1}$ (CHCl_3) 2251, 1704, 1467, 1424, 1340; m/z (EI) calcd. for $\text{C}_{20}\text{H}_{15}\text{NO}$ 285.1154; found 285.1151.

Annulation Product 16h

Synthesized from 4-(2-bromo-phenyl)-1-methyl-1H-pyrrole-3-carboxylic acid ethyl ester **6h** and norbornadiene (4 equiv.) at 120 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 7:1) yielding the title compound as a colorless oil (51.0 mg, 100%);

R_f = 0.30 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, $CDCl_3$) 9.75 (1H, d, J = 8.9), 7.89 (1H, d, J = 8.9), 7.82 (1H, s), 7.67 (1H, d, J = 9.3), 7.64-7.59 (1H, m), 7.48-7.44 (1H, m), 7.40 (1H, d, J = 9.3), 4.40 (1H, q, J = 7.0), 3.82 (3H, s), 1.42 (3H, t, J = 7.0); δ_C (75 MHz, $CDCl_3$) 165.3, 134.8, 134.7, 130.5, 128.8, 128.5, 127.2, 126.2, 125.0, 124.3, 121.5, 110.7, 109.8, 60.1, 33.8, 14.8; ν_{max}/cm^{-1} ($CHCl_3$) 2980, 2252, 1700, 1530, 1517, 1424, 1406; m/z (EI) calcd. for $C_{16}H_{15}NO_2$ 253.1103; found 253.1107.

Annulation Product 16i

Synthesized from 3-(2-bromo-phenyl)-1-methyl-1H-pyrrole **6i** and norbornadiene (4 equiv.) at 120 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (40.3 mg, 86%); R_f = 0.55 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, $CDCl_3$) 8.22, (1H, d, J = 8.3), 7.89 (1H, d, J = 8.3), 7.61 (1H, d, J = 8.8), 7.56-7.48

(2H, m), 7.40 (1H, t, J = 7.1), 7.11 (1H, d, J = 2.9), 7.01 (1H, d, J = 2.9), 3.90 (3H, s); δ_C (75 MHz, $CDCl_3$) 133.3, 120.1, 128.7, 128.6, 127.0, 125.9, 123.6, 123.4, 123.1, 122.7, 111.2, 100.5, 33.4; ν_{max}/cm^{-1} ($CHCl_3$) 2980, 2252, 1700, 1530, 1517, 1424, 1406; m/z (EI) calcd. for $C_{13}H_{11}N$ 181.0891; found 181.0888.

Annulation Product 16j¹⁰

Synthesized from 1-(2-bromo-phenyl)-1H-indole **6j** and norbornadiene (4 equiv.) at 120 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (30.3 mg, 70%); R_f = 0.65 (hexane:ethyl acetate, 2:1); δ_H (300

MHz, $CDCl_3$) 8.56 (1H, d, J = 8.3), 8.45 (1H, d, J = 7.3), 7.86 (1H, d, J = 7.0), 7.64-7.57 (2H, m), 7.44-7.29 (4H, m), 7.11 (1H, d, J = 9.4), 6.79 (1H, s), data identical to those previously reported.¹⁰

Annulation Product 15b

Synthesized from 1-(2-bromo-phenyl)-1H-pyrrole **6b** and norbornadiene (4 equiv.) at 80 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (18.7 mg, 40%); R_f = 0.50 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, C_6D_6) 6.69 (1H, d, J = 7.6), 6.66-6.64 (1H, m), 6.55 (1H, d, J = 7.0), 6.57-6.46 (2H, m), 6.06 (1H, t, J = 3.1), 5.76-5.74 (1H, m), 5.66 (2H, s), 2.53-2.51 (2H, m), 2.34 (1H, s), 2.22 (1H, d, J = 9.4), 0.86 (1H, d, J = 8.8), 0.74 (1H, d, J = 8.8); δ_C (75 MHz, C_6D_6) 137.1, 137.0, 135.3, 131.3, 130.6, 126.9, 123.5, 118.8, 114.0, 113.0, 111.3, 107.5, 54.3, 54.2, 43.9, 39.5, 35.8; ν_{max}/cm^{-1} ($CHCl_3$) 2252, 1709, 1505, 1472, 1330; m/z (EI) calcd. for $C_{17}H_{15}N$ 233.1205; found 233.1202.

Annulation Product 18

Synthesized from 1-(2-bromo-phenyl)-1H-pyrrole **6b** and norbornadiene (4 equiv.) at 80 °C according to the general procedure. Purified by flash column chromatography (hexane:DCM, 20:1) yielding the title compound as a colorless oil (18.8 mg, 40%); R_f = 0.65 (hexane:DCM, 2:1); δ_H (300 MHz, $CDCl_3$) 6.80-6.76 (2H, m), 6.68-6.57 (2H, m), 6.33 (2H, d, J = 6.4), 6.07 (2H, s), 5.61 (1H, dd, J = 5.1, 3.0), 5.55 (1H, dd, J = 5.1, 3.0), 2.67 (1H, d, J = 3.9), 2.54 (1H, d, J = 3.9), 2.29 (1H, s), 2.17 (1H, s), 0.82 (1H, d, J = 9.3), 0.57 (1H, d, J = 9.3); δ_C (75 MHz, $CDCl_3$) 148.1, 136.5, 136.3, 134.7, 133.6, 129.1, 118.7, 118.2, 116.3, 110.8, 47.9, 47.3, 41.9, 41.7, 41.5, 41.2; ν_{max}/cm^{-1} ($CHCl_3$) 2252, 1710, 1601, 1500; m/z (EI) calcd. for $C_{17}H_{15}N$ 233.1205; found 233.1202.

Annulation Product 15c

Synthesized from 1-(2-bromo-4-fluoro-phenyl)-1H-pyrrole **6c** and norbornadiene (4 equiv.) according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 20:1) yielding the title compound as a colorless oil (38.6 mg, 77%); R_f = 0.60 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, C_6D_6) 6.71-6.69 (2H, m), 6.45 (1H, dd, J = 8.9, 3.4), 6.35 (1H, dd, J = 8.9, 7.6), 6.15-6.13 (2H, m), 5.59 (1H, dd, J = 5.8, 3.0), 5.54 (1H, dd, J = 5.8, 3.0), 2.59 (2H, s), 2.34 (1H, s), 2.28 (1H, s), 0.86 (1H, d, J = 9.4), 0.59 (1H, d, J = 9.4); δ_C (75 MHz, $CDCl_3$) 155.0, 151.7, 136.8, 136.4, 135.9, 131.7, 131.5, 122.2, 120.7, 119.0, 115.9, 115.6, 114.6, 110.8, 109.8, 47.7, 44.8, 41.5, 41.2, 41.1; ν_{max}/cm^{-1} ($CHCl_3$) 2976, 2252, 1710, 1504, 1335; m/z (EI) calcd. for $C_{17}H_{16}NF$ 251.1110; found 251.1115.

Annulation Product 15e

Synthesized from 1-(2-bromo-4-methyl-phenyl)-1H-pyrrole-2-carbaldehyde **6e** and norbornadiene (4 equiv.) at 80 °C according to the general procedure. Purified by flash column chromatography (hexane:ethyl acetate, 10:1) yielding the title compound as a colorless oil (26.8 mg, 64%); R_f = 0.55 (hexane:ethyl acetate, 2:1); δ_H (300 MHz, $CDCl_3$) 9.54 (1H, s), 8.24 (1H, d, J = 8.6), 7.19 (1H, d, J = 4.1), 7.13 (1H, s), 7.06 (1H, d, J = 8.6), 6.40 (1H, dd, J = 6.1, 3.0), 6.31 (1H, dd, J = 6.1, 3.0), 6.27 (1H, d, J = 4.1), 3.13 (1H, d, J = 9.4), 3.06 (2H, s), 2.91 (1H, d, J = 9.4), 2.34 (3H, s), 1.28 (2H, s); δ_C (75 MHz, $CDCl_3$) 177.2, 145.8, 138.6, 136.7, 135.4, 132.4, 132.1, 131.9, 130.7, 128.5, 127.9, 120.2, 109.5, 54.7, 44.2, 40.1, 37.2, 20.9; ν_{max}/cm^{-1} ($CHCl_3$) 2978.1, 2252, 1659, 1507, 1573; m/z (+ESI) calcd. for $C_{19}H_{17}NONa$ 298.1202: 298.1, found 298.1212.

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Spectra

1-(2-Bromo-4-methyl-phenyl)-1H-pyrrole (6a)

1-(2-Bromo-4-fluoro-phenyl)-1H-pyrrole (6c)

1-(2-Bromo-4-chloro-phenyl)-1H-pyrrole (6d)

1-(2-Bromo-4-methyl-phenyl)-1H-pyrrole-2-carbaldehyde (6e)

1-(2-Bromo-4-methyl-phenyl)-3-methyl-1H-pyrrole (6f R = Me)

1-(2-Bromo-4-methyl-phenyl)-3-phenyl-1H-pyrrole-2-carbaldehyde (6g)

4-(2-Bromo-phenyl)-1H-pyrrole-3-carboxylic acid ethyl ester

4-(2-Bromo-phenyl)-1-methyl-1H-pyrrole-3-carboxylic acid ethyl ester (6h)

3-(2-Bromo-phenyl)-1-methyl-1H-pyrrole (6i)

1-(2-Bromo-phenyl)-1H-indole (6j)

Annulation Product 5

Annulation Product 6a

Annulation Product 6b

Annulation Product 6c

Annulation Product 6d

Annulation Product 6e

Annulation Products 6f and 6g ($R = Me$)

Annulation Products 6f and 6g (R = Ph)

Annulation Product 6h

Annulation Product 6i

Annulation Product 6j

Annulation Product 9

Annulation Product 11

Annulation Product 13

Annulation Product 15a

Annulation Product 16a

Annulation Product 16c

Annulation Product 16d

Annulation Product 16e

Annulation Product 16g

Annulation Product 16h

Annulation Product 16i

Annulation Product 15b

Annulation Product 18

Annulation Product 15c

Annulation Product 15e