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Supporting Information

Supporting Information for:

Dioxomolydenum(VI)-Catalyzed Reductive Cyclization of Nitroaromatics. Synthesis of Carbazoles and Indoles

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General Considerations:

All reactions involving air-sensitive compounds were carried out under N_2 atmosphere in oven-dried glassware with magnetic stirring. Dry THF and toluene were continuously refluxed and freshly distilled under nitrogen from sodium and potassium respectively. Dry acetonitrile and dichlorometane were continuously refluxed and freshly distilled from P_2O_5 under nitrogen. Solvents used in extraction and purification were distilled prior to use. TLC was performed on aluminabacked plates coated with silica gel 60 with F_{254} indicator; the chromatograms were visualized by UV light (254 nm) and/or by staining with a Ce/Mo reagent, anisaldehyde or phosphomolybdic acid solution and subsequent heating. R_f values refer to silica gel. Flash column chromatography was carried out on silica gel 60, 230-400 mesh (Merck). Melting points were obtained on a Büchi-Tottoli apparatus using open capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-Plus 300 spectrometer. ^{1}H NMR spectra were recorded at 300 or 400 MHz. Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26; CD_3SOCHD_2: δ 2.50; CD_3COCHD_2: δ 2.05). Data are reported as follows: chemical shift, multiplicity (s: singlet, br s: broad singlet, d: doublet, dd: doublet of doublets, dt: doublet of triplets, t: triplet, td: triplet of doublets, q: quartet, m: multiplet), coupling constants (*J* in Hz) and integration. ^{13}C NMR spectra were recorded at 75.4 or 100.6 MHz using broadband proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as internal standard ($CDCl_3$: δ 76.95; DMSO-d_6: δ 39.52; acetone-d_6: δ 29.84). Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on a Agilent 6890N/5973 or Micromass Autospec spectrometer and only the molecular ions and/or base peaks in MS are given. High-resolution mass spectrometry (HRMS) was carried out on a Micromass Autospec spectrometer. All commercially available reagents were used without purification unless otherwise indicated and were purchased from standard chemical suppliers. $Na_2MoO_4.2H_2O$ to prepare the catalyst was obtained from Acros Organics, and triphenylphosphine polymer-bound, (200-400 mesh, loading: 3 mmol/g) was purchased from Fluka. $MoO_2Cl_2(dmf)_2$ was prepared as previously described by us.[1] 4,4´-Di-*t*-butyl-2-nitrobiphenyl **1b** was synthesized by nitration of DTBB.[2] 2-Nitrobiphenyl derivatives **1c-g** were prepared via Suzuki-Miyaura cross-coupling following a reported procedure.[2] 4-Hydroxy-2-nitrobiphenyl **1h** was prepared by demethylation of **1c** with BBr_3.[2] 2-Nitrobiphenyl-4-carboxylic acid **1i** was obtained from **1g** by alkaline hydrolysis.[2] Although it is commercially available (Sigma, C4753), 4-chloro-2-nitrobenzaldehyde **7d** was prepared by MnO_2 oxidation of 4-chloro-2-nitrobenzyl alcohol in 66% yield and characterized as a white solid: mp 67-69ºC; ^{1}H NMR ($CDCl_3$, 300 MHz, 25ºC): d 10.31 (s, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.74 (dd, *J* = 8.3, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25ºC): d 186.8 (CH), 140.0 (C), 135.6 (C), 134.0 (CH), 130.7 (CH), 129.1 (C), 124.6 (CH); EI-LRMS *m/z* 187 (M^++2, 0.5), 185 (M^+, 1), 75 (100).

Typical Procedure for the Reductive Cyclization of 2-Nitrobiphenyls 1 and 2-Nitrostyrenes 5 with PPh_3 Catalyzed by $MoO_2Cl_2(dmf)_2$:

To a solution of the corresponding 2-nitrobiphenyl derivative **1a-i** (1 mmol) or 2-nitrostyrene **5a-e** (1 mmol) and PPh_3 (629 mg, 2.4 mmol) in dry toluene (10 mL), $MoO_2Cl_2(dmf)_2$ (17.3 mg, 0.05 mmol) was added, and the resulting mixture was stirred under nitrogen at reflux for 16 h (overnight). The excess of PPh_3 was oxidized by adding DMSO (0.5 mL) and $MoO_2Cl_2(dmf)_2$ (3.5 mg, 0.01 mmol) to the reaction mixture and stirring at reflux for 30 min. The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford the corresponding carbazoles **3a-i** and indoles **6a-e**:

Carbazole (3a): Reaction of **1a** (199 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 20/1) on silica gel, gave 139 mg (83%) of **3a** as a white solid: mp 243-245ºC; ^{1}H NMR ($CDCl_3$, 300 MHz, 25ºC): d 8.09 (d, *J* = 7.8 Hz, 2H), 8.05 (br s, 1H), 7.45-7.41 (m, 4H), 7.28-7.21 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25ºC): d 139.4 (C), 125.7 (CH), 123.2 (C), 120.2 (CH), 119.3 (CH), 110.5 (CH); EI-LRMS *m/z* 167 (M^+,100). Spectroscopic data and analytical characterization are consistent with a commercially available sample.

2,7-Di-*tert*-butylcarbazole (3b): Reaction of **1b** (311 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 20/1) on silica gel, gave 223 mg (80%) of **3b** as a white solid: mp 151-153ºC (lit.[3] mp 155-156ºC); ^{1}H NMR ($CDCl_3$, 300 MHz, 25ºC): d 7.98 (d, *J* = 8.3 Hz, 2H), 7.86 (br s, 1H), 7.43 (s, 2H), 7.32 (dd, *J* = 8.3, 1.4 Hz, 2H), 1.46 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25ºC): d 148.8 (C), 139.9 (C), 120.8 (C), 119.4 (CH), 117.2 (CH), 107.0 (CH), 35.0 (C), 31.7 (CH_3); EI-LRMS *m/z* 279 (M^+, 41), 264 (100); HRMS calcd for $C_{20}H_{25}N$ 279.1987, found 279.1983. Spectroscopic data and analytical characterization are consistent with the literature.[3]

2-Methoxycarbazole (3c): Reaction of **1c** (229 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 5/1) on silica gel, gave 154 mg (78%) of **3c** as a white solid: mp 229-231ºC (lit.[4] mp 233ºC); ^{1}H NMR ($CDCl_3$+DMSO-d_6, 300 MHz, 25ºC): d 10.86 (br s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.37(d, *J* = 8.0 Hz, 1H), 7.27-7.20 (m, 1H), 7.10-7.03 (m, 1H) 6.92 (d, *J* = 2.0 Hz, 1H), 6.71 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$+DMSO-d_6, 75.4 MHz, 25ºC): d 156.8 (C), 139.4 (C), 138.1 (C), 122.3 (CH), 121.0 (C), 118.9 (CH), 117.3 (CH), 116.8 (CH), 114.6 (C), 108.8 (CH), 105.9 (CH), 92.7 (CH), 53.5 (CH_3); EI-LRMS *m/z* 197 (M^+, 100); HRMS calcd for $C_{13}H_{11}NO$ 197.0841, found 197.0845. Spectroscopic data and analytical characterization are in consistent with the literature.[4,5]

2-Formylcarbazole (3d): Reaction of **1d** (227 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 10/1) on silica gel, gave 137 mg (70%) as a brown solid: mp 145-147ºC (lit.[6] mp 155ºC); ^{1}H NMR (acetone-d_6, 300 MHz, 25ºC): d 10.84 (br s, 1H), 10.13 (s, 1H), 8.30 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 8.09 (s, 1H), 7.76 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.52-7.47 (m, 1H), 7.27-7.23 (m, 1H); ^{13}C NMR (acetone-d_6, 75.4 MHz, 25ºC): d 193.0 (C), 142.7 (C), 140.4 (C), 135.2 (C), 128.8 (C), 128.2 (CH), 123.0 (C), 122.0 (CH), 121.2 (CH), 120.6 (CH), 120.4 (CH), 113.7 (CH), 112.2 (CH); EI-LRMS *m/z* 195 (M^+, 100); HRMS calcd for $C_{13}H_9NO$ 195.0684, found 195.0689. Spectroscopic data and analytical characterization are consistent with the literature.[2,6]

2-Acetylcarbazole (3e): Reaction of **1e** (241 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 5/1) on silica gel, gave 169 mg (81%) as a pale yellow solid: mp 230-232ºC (lit.[7] mp 234-236ºC); ^{1}H NMR (DMSO-d_6, 300 MHz, 25ºC): d 11.58 (br s, 1H), 8.23-8.16 (m, 2H), 8.12 (s, 1H), 7.79 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.51-7.44 (m, 1H), 7.25-7.17 (m, 1H), 2.67 (s, 3H); ^{13}C NMR (DMSO-d_6, 75.4 MHz, 25ºC): d 198.0 (C), 141.4 (C), 139.2 (C), 134.1 (C), 127.1 (CH), 126.2 (C), 121.7 (C), 121.2 (CH), 119.2 (CH), 118.8 (CH), 111.5 (CH), 111.4 (CH), 27.1 (CH_3); EI-LRMS *m/z* 209 (M^+, 71), 194 (100); HRMS calcd for $C_{14}H_{11}NO$ 209.0841, found 209.0836. Spectroscopic data and analytical characterization are consistent with the literature.[2,7]

2-Fluorocarbazole (3f): Reaction of **1f** (217 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 20/1) on silica gel, gave 135 mg (73%) as a white solid: mp 190-192ºC (lit.[8] mp 221ºC); ^{1}H NMR (acetone-d_6, 300 MHz, 25ºC) d 10.50 (br s, 1H), 8.13-8.06 (m, 2H), 7.51 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.43 (ddd, *J* = 8.1, 7.2, 1.2 Hz, 1H), 7.24 (dd, *J* = 10.0, 2.2 Hz, 1H), 7.19 (ddd, *J* = 7.9, 7.2, 1.1 Hz, 1H), 6.96 (ddd, *J* = 9.9, 8.6, 2.2 Hz, 1H); ^{13}C NMR (acetone-d_6, 300 MHz, 25ºC) d 162.7 (d, *J* = 239 Hz, C), 141.5 (C), 12.1 (CH), 123.5 (C), 122.0 (d, *J* = 10.7 Hz, CH), 120.6 (CH), 120.1 (CH), 111.7 (CH), 107.5 (d, *J* = 24.4 Hz, CH), 98.1 (d, *J* = 26.5 Hz, CH); EI-LRMS *m/z* 185 (M^+, 100); HRMS calcd for $C_{12}H_8FN$ 185.0641, found 185.0644. Spectroscopic data and analytical characterization are consistent with the literature.[2,8]

Ethyl carbazole-2-carboxylate (3g): Reaction of **1g** (271 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 20/1) on silica gel, gave 208 mg (87%) as a white solid: mp 174-176ºC (lit.[9] mp 184ºC); ^{1}H NMR (DMSO-d_6, 300 MHz, 25ºC): d 11.60 (br s, 1H), 8.25-8.11 (m, 3H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.65-7.58 (m, 1H), 7.52-7.44 (m, 1H), 7.25-7.16 (m, 1H), 4.35 (q, *J* 7.0 Hz, 2H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (DMSO-d_6, 75.4 MHz, 25ºC): d 166.5 (C), 141.2 (C), 139.2 (C), 127.0 (CH), 126.7 (C), 126.3 (CH), 121.8 (C), 121.1 (CH), 120.0 (CH), 119.3 (C), 119.2 (CH), 112.4 (CH), 111.5 (CH), 60.6 (CH_2), 14.3 (CH_3); EI-LRMS *m/z* 239 (M^+, 100); HRMS calcd for $C_{15}H_{13}NO_2$ 239.0946, found 239.0940. Spectroscopic data and analytical characterization are consistent with the literature.[9,10]

2-Hydroxycarbazole (3h): Treatment of **1h** (215 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 20/1) on silica gel, gave 60 mg (33%) as a white solid: mp 270-272ºC (lit.[11] mp 262-264ºC); ^{1}H NMR (DMSO-d_6, 300 MHz, 25ºC): d 10.94 (br s, 1H), 9.43 (br s, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 7.9, 1H), 7.27-7.23 (m, 1H), 7.10-7.03 (m, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 6.64 (dd, *J* = 8.4, 2.0 Hz, 1H); ^{13}C NMR (DMSO-d$_6$, 75.4 MHz, 25ºC): d 156.5 (C), 141.5 (C), 139.6 (C), 123.8 (CH), 123.0 (C), 120.9 (CH), 119.0 (CH), 118.4 (CH), 115.3 (C), 110.4 (CH), 108.4 (CH), 96.4 (CH); HRMS calcd for $C_{12}H_9NO$ 183.0684, found 183.0674. Spectroscopic data and analytical characterization are consistent with a commercially available sample.

Carbazole-2-carboxylic acid (3i): Treatment of **1i** (243 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 1/1) on silica gel, gave 63 mg (30%) as a white solid: mp > 300ºC (dec.) [lit.[9] mp 322ºC (dec.)]; ^{1}H NMR (DMSO-d$_6$, 300 MHz, 25ºC): d 11.52 (br s, 1H), 8.22-8.15 (m, 2H), 8.09 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.57-7.42 (m, 3H), 7.24-7.17 (m, 1H); ^{13}C NMR (DMSO-d$_6$, 75.4 MHz, 25ºC): d 169.0 (C), 141.9 (C), 140.0 (C), 128.5 (C), 127.8 (CH), 126.8 (C), 122.6 (CH), 122.0 (CH), 120.9 (CH), 120.5 (CH), 120.0 (CH), 113.4 (CH), 112.3 (CH); HRMS calcd for $C_{13}H_9NO_2$ 211.0633, found 211.0632.

2-Phenyl-1*H*-indole (6a): Reaction of **5a** (as a 4/1 *E*/*Z* mixture) (225 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 7/1) on silica gel, gave 141 mg (73%) of **6a** as a white solid: mp 190-192ºC; ^{1}H NMR (CDCl$_3$, 300 MHz, 25ºC): d 8.41 (br s, 1H), 7.70-7.64 (m, 3H), 7.49-7.30 (m, 4H), 7.26-7.09 (m, 2H), 6.85 (s, 1H); ^{13}C NMR (CDCl$_3$, 75.4 MHz, 25ºC): d 137.8 (C), 136.7 (C), 132.2 (C), 129.1 (C), 128.9 (CH), 127.6 (CH), 125.1 (CH), 122.2 (CH), 120.5 (CH), 120.1 (CH), 110.8 (CH), 99.8 (CH); EI-LRMS *m/z* 193 (M^+, 100). Spectroscopic data and analytical characterization are consistent with a commercially available sample.

2-Pentyl-1*H*-indole (6b): Treatment of **5b** (0.219 g, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 7/1) on silica gel, gave 150 mg (80%) of **6b** as a white solid: mp 40-42ºC(lit.[12] mp 44-44.5ºC); ^{1}H NMR (CDCl$_3$, 300 MHz, 25ºC): d 7.83 (br s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.14 (dt, *J*= 7.1, 1.4 Hz, 1H), 7.09 (dt, *J* = 7.2, 1.4 Hz, 3H), 6.26 (s, 1H), 2.75 (t, *J* = 7.7 Hz, 2H), 1.80-1.69 (m, 2H), 1.45-1.35 (m, 4H), 0.98-0.89 (m, 3H); ^{13}C NMR (CDCl$_3$, 75.4 MHz, 25ºC): d 140.0 (C), 135.6 (C), 128.6 (C), 120.6

(CH), 119.5 (CH), 119.3 (CH), 110.3 (CH), 99.0 (CH), 31.4 (CH_2), 28.7 (CH_2), 27.9 (CH_2), 22.4 (CH_2), 13.9 (CH_3); EI-LRMS *m/z* 187 (M^+, 34), 130 (100); HRMS calcd for $C_{13}H_{17}N$ 187.1361, found 187.1356. Spectroscopic data and analytical characterization are consistent with the literature.[12]

2-Methyl-1*H*-indole (6c): Treatment of **5c** (163 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 7/1) on silica gel, gave 101 mg (77%) of **6c** as a white solid: mp 58-60ºC; ^1H NMR ($CDCl_3$, 300 MHz, 25ºC): d 7.75 (br s, 1H), 7.59-7.54 (m, 1H), 7.30-7.25 (m, 1H), 7.19-7.09 (m, 2H), 6.26 (s, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25ºC): d 135.9 (C), 135.0 (C), 128.9 (C), 120.8 (CH), 119.5 (CH), 110.1 (CH), 100.2 (CH), 13.6 (CH_3); EI-LRMS *m/z* 131 (M^+, 66), 130 (100). Spectroscopic data and analytical characterization are consistent with a commercially available sample.

Ethyl 1*H*-indole-2-carboxylate (6d): Treatment of **5d** (221 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 7/1) on silica gel, gave 142 mg (75%) of **6d** as a white solid: mp 121-123ºC; ^1H NMR ($CDCl_3$, 300 MHz, 25ºC): d 9.46 (br s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.37-7.31 (m, 1H), 7.27 (s, 1H), 7.20-7.14 (m, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25ºC): d 162.3 (C), 136.9 (C), 127.3 (C), 125.2 (CH), 122.4 (CH), 120.6 (CH), 111.9 (CH), 108.5 (CH), 61.0 (CH_2), 14.3 (CH_3); EI-LRMS *m/z* 189 (M^+, 38), 143 (100). Spectroscopic data and analytical characterization are consistent with a commercially available sample.

Ethyl 3-methyl-1*H*-indole-2-carboxylate (6e): Treatment of **5e** (235 mg, 1 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 7/1) on silica gel, gave 171 mg (84%) as a white solid: mp 128-130 ºC (lit.[13] mp 127-128 ºC); ^1H NMR ($CDCl_3$, 300 MHz, 25 ºC): d 9.09 (br s, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.42-7.32 (m, 2H), 7.20-7.14 (m, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 2.65 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25 ºC): d 162.7 (C), 135.8 (C), 128.4 (C), 125.4 (CH), 123.3 (C), 120.6 (CH), 119.9 (C), 119.7 (CH), 111.6 (CH), 60.6 (CH_2), 14.3 (CH_3), 9.9 (CH_3); EI-LRMS *m/z* 203 (M^+, 53), 157 (100); HRMS calcd for $C_{12}H_{13}NO_2$ 203.0946, found 203.0955. Spectroscopic data and analytical characterization are consistent with the literature.[13]

Typical Procedure for the Synthesis of Indole Derivatives 6d,f-o by One Pot, Sequential Wittig Reaction-Reductive Cyclization of 2-Nitrobenzaldehydes 7.

To a solution of the corresponding 2-nitrobenzaldehyde **7** (2 mmol) in dry toluene (20 mL), the corresponding phosphorane **8** (2 mmol) was added at room temperature, and the resulting mixture was stirred at this temperature for 1-2 h. Consumption of the starting aldehyde and generation of the corresponding 2-nitrocinammate or 2-nitrochalcone was monitored by GC-MS. PPh_3 (1.26 g, 4.8 mmol) and $MoO_2Cl_2(dmf)_2$ (34.5 mg, 0.10 mmol) were added and the resulting mixture was stirred under nitrogen at reflux for 12 h. Then, another batch of $MoO_2Cl_2(dmf)_2$ (34.5 mg, 0.10 mmol) was added and the stirring at reflux continued for another 12 h. The excess of PPh_3 was oxidized by adding DMSO (1.0 mL) and $MoO_2Cl_2(dmf)_2$ (6.9 mg, 0.02 mmol) to the reaction mixture and stirring at reflux for 30 min. The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford the corresponding indoles **6d,f-o**:

Ethyl 4-chloro-1*H*-indole-2-carboxylate (6f): Reaction of 6-chloro-2-nitrobenzaldehyde (371 mg, 2 mmol) with (carbethoxymethylene)triphenylphosphorane **8a** (697 mg, 2 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 7/1) on silica gel, gave 380 mg (85%) of **6f** as a white solid: mp 140-142ºC (lit.[14] mp 143ºC); ^{1}H NMR ($CDCl_3$, 300 MHz, 25ºC): d 9.54 (br s, 1H), 7.36-7.31 (m, 2H), 7.26-7.19 (m, 1H), 7.17-7.13 (m, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25ºC): d 162.0 (C), 137.3 (C), 127.7 (C), 127.7 (C), 126.5 (C), 125.7 (CH), 120.3 (CH), 110.5 (CH), 106.9 (CH), 61.3 (CH_2), 14.3 (CH_3); EI-LRMS *m/z* 225 (M^++2, 20), 223 (M^+, 52), 177 (100); HRMS calcd for $C_{11}H_{10}ClNO_2$ 223.0400, found 223.0410. Spectroscopic data and analytical characterization are consistent with the literature.[14,15]

Ethyl 5-chloro-1*H*-indole-2-carboxylate (6g): Reaction of 5-chloro-2-nitrobenzaldehyde (371 mg, 2 mmol) with (carbethoxymethylene)triphenylphosphorane **8a** (697 mg, 2 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 10/1) on silica gel, gave 67 mg (15%) of **6g** as a white solid: mp 167-169ºC (lit.[16] mp 171.5-172.5ºC); ^{1}H NMR ($CDCl_3$, 300 MHz, 25ºC): d 9.22 (br s, 1H), 7.66 (s, 1H), 7.38-7.32 (m, 1H), 7.29-7.24 (m, 1H), 7.15 (s, 1H), 4.43 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25ºC): d 161.8 (C), 135.0 (C), 128.6 (C), 128.3 (C), 126.3 (C), 125.7 (CH), 121.6 (CH), 113.0 (CH), 107.9 (CH), 61.2 (CH_2), 14.3 (CH_3); EI-LRMS *m/z* 225 (M^++2, 16), 223 (M^+, 48), 177 (100); HRMS calcd for $C_{11}H_{10}ClNO_2$ 223.0400, found 223.0402. Spectroscopic data and analytical characterization are consistent with the literature.[16,17]

Ethyl 6-chloro-1*H*-indole-2-carboxylate (6h): Reaction of 4-chloro-2-nitrobenzaldehyde (371 mg, 2 mmol) with (carbethoxymethylene)triphenylphosphorane **8a** (697 mg, 2 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 5/1) on silica gel, gave 224 mg (50%) of **6h** as a white solid: mp 163-165ºC (lit.[18a] mp 182-184ºC); ^{1}H NMR (acetone-d_6, 300 MHz, 25ºC): d 11.14 (br s, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.57 (s, 1H), 7.19 (s, 1H), 7.11 (dd, J = 8.5, 1.9 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (acetone-d_6, 75.4 MHz, 25ºC): d 161.9 (C), 138.6 (C), 130.9 (C), 129.7 (C), 126.9 (C), 124.4 (CH), 121.9 (CH), 112.8 (CH), 108.7 (CH), 61.4 (CH_2), 14.6 (CH_3); EI-LRMS *m/z* 225 (M^++2, 18), 223 (M^+, 62), 177 (100); HRMS calcd for $C_{11}H_{10}ClNO_2$ 223.0400, found 223.0410. Spectroscopic data and analytical characterization are consistent with the literature.[18]

Ethyl 5*H*-[1,3]dioxolo[4,5-*f*]indole-6-carboxylate (6i): Treatment of 6-nitropiperonal (390 mg, 2 mmol) with (carbethoxymethylene)triphenylphosphorane **8a** (697 mg, 2 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 4/1) on silica gel, gave 378 mg (81%) of **6i** as a white solid: mp 175-177ºC (lit.[19] mp 175-178ºC); ^{1}H NMR (acetone-d_6, 300 MHz, 25ºC): d 10.79 (br s, 1H), 7.05 (s, 1H), 7.02 (s, 1H), 6.95 (s, 1H), 5.98 (s, 2H), 4.31 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (acetone-d_6, 75.4 MHz, 25ºC): d 161.9 (C), 148.5 (C), 144.9 (C), 134.2 (C), 127.3 (C), 122.4 (C), 109.1 (CH), 101.8 (CH_2), 100.1 (CH), 92.7 (CH), 60.9 (CH_2), 14.7 (CH_3); EI-LRMS *m/z* 233 (M^+, 78), 187 (100); HRMS calcd for $C_{12}H_{11}NO_4$ 233.0688, found 233.0684. Spectroscopic data and analytical characterization are consistent with the literature.[19]

Ethyl 7-methoxy-1*H*-indole-2-carboxylate (6j): Reaction of 3-methoxy-2-nitrobenzaldehyde (362 mg, 2 mmol) with (carbethoxymethylene)triphenylphosphorane **8a** (697 mg, 2 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 5/1) on silica gel, gave 197 mg (45%) of **6j**, 125 mg (25%) of ethyl 3-methoxy-2-nitrocinnamate, and 44 mg (10%) of ethyl 2-amino-3-methoxycinnamate. Indole **6j** was isolated as a white solid: mp 160-162ºC (lit.[18a] mp 115-117ºC); ^{1}H NMR ($CDCl_3$, 300 MHz, 25ºC): d 9.13 (br s, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 2.3 Hz, 1H), 7.10-7.03 (m, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.97 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25ºC): d 161.7 (C), 146.3 (C), 128.5 (C), 127.9 (C), 127.1 (C), 121.0 (CH), 114.7 (CH), 108.7 (CH), 103.9 (CH), 60.9 (CH_2), 55.3 (CH_3), 14.3 (CH_3); EI-LRMS *m/z* 219 (M^+, 100); HRMS calcd for $C_{12}H_{13}NO_3$ 219.0895, found 219.0894. Spectroscopic data and analytical characterization are consistent with the literature.[17,18a]

Ethyl 3-methoxy-2-nitrocinnamate: white solid: mp 71-73ºC; ^{1}H NMR ($CDCl_3$, 300 MHz, 25ºC): d 7.51-7.38 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25ºC): d 165.4 (C), 150.8 (C), 140.8 (C), 136.0 (CH), 131.0 (CH), 127.8 (C), 123.6 (CH), 118.4 (CH), 113.6 (CH), 60.8 (CH_2), 56.4 (CH_3), 14.1 (CH_3); EI-LRMS *m/z* 251 (M^+, 3), 177 (100).

Ethyl 2-amino-3-methoxycinnamate: yellow oil. R_f 0.29 (5/1, hexane/AcOEt); ^{1}H NMR ($CDCl_3$, 300 MHz, 25ºC): d 7.84 (d, *J* = 15.8 Hz, 1H), 7.02 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.78 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.70 (t, *J* = 7.9 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.21 (br s, 2H), 3.86 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz, 25ºC): d 167.3 (C), 147.5 (C), 139.8 (CH), 136.0 (C), 119.6 (CH), 119.5 (C), 118.0 (CH), 117.7 (CH), 111.0 (CH), 60.3 (CH_2), 55.6 (CH_3), 14.3 (CH_3); EI-LRMS *m/z* 221 (M^+, 37), 176 (100).

2-Acetyl-1*H*-indole (6k): Reaction of 2-nitrobenzaldehyde (302 mg, 2 mmol) with 1-(triphenylphosphoranylidene)-2-propanone **8b** (637 mg, 2 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 5/1) on silica gel, gave 201 mg (63%) of **6k** as a white solid: mp 151-153ºC (lit.[17] mp 152-154ºC); ^{1}H NMR (CDCl$_3$, 400 MHz, 25ºC): d 9.23 (br s, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.38-7.33 (m, 1H), 7.22 (d, *J* = 2.2 Hz, 1H), 7.18-7.13 (m, 1H), 1.61 (s, 3H); ^{13}C NMR (CDCl$_3$, 100.6 MHz, 25ºC): d 190.6 (C), 137.4 (C), 135.3 (C), 127.4 (CH), 126.3 (CH), 122.9 (CH), 120.8 (CH), 112.2 (CH), 109.9 (CH), 25.8 (CH$_3$); EI-LRMS *m/z* 159 (M$^+$, 88), 144 (100); HRMS calcd for $C_{10}H_9NO$ 159.0684, found 159.0687. Spectroscopic data and analytical characterization are consistent with the literature.[17,20]

2-Acetyl-4-chloro-1*H*-indole (6l):[21] Reaction of 6-chloro-2-nitrobenzaldehyde (371 mg, 2 mmol) with 1-(triphenylphosphoranylidene)-2-propanone **8b** (637 mg, 2 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 5/1) on silica gel, gave 360 mg (93%) of **6l** as a white solid: mp 148-150ºC; ^{1}H NMR (CDCl$_3$, 300 MHz, 25ºC): d 9.66 (br s, 1H), 7.36 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.30 (dd, *J* = 2.3, 1.0 Hz, 1H), 7.25 (t, *J* = 7.9 Hz, 1H), 7.15 (dd, *J* = 7.5, 1.0 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (CDCl$_3$, 75.4 MHz, 25ºC): d 190.6 (C), 137.8 (C), 135.4 (C), 128.1 (C), 126.7 (CH), 126.6 (C), 120.4 (CH), 110.9 (CH), 108.1 (CH), 25.9 (CH$_3$); EI-LRMS *m/z* 195 (M$^+$+2, 31), 193 (M$^+$, 78), 178 (100); HRMS calcd for $C_{10}H_8ClNO$ 193.0294, found 193.0296.

2-Acetyl-5-chloro-1*H*-indole (6m): Reaction of 5-chloro-2-nitrobenzaldehyde (371 mg, 2 mmol) with 1-(triphenylphosphoranylidene)-2-propanone **8b** (637 mg, 2 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 5/1) on silica gel, gave 151 mg (39%) of **6m** as a white solid: mp 200-202ºC (lit.[22] mp 206-207ºC); ^{1}H NMR (acetone-d$_6$, 300 MHz, 25ºC): d 10.98 (br s, 1H), 7.74 (d, *J* = 1.9 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.31-7.26 (m, 2H), 2.56 (s, 3H); ^{13}C NMR (acetone-d$_6$, 75.4 MHz, 25ºC): d 190.5 (C), 138.0 (C), 136.9 (C), 129.4 (C), 126.5 (CH), 126.3 (C), 122.6 (CH), 114.9 (CH), 109.2 (CH), 26.1 (CH$_3$); EI-

LRMS *m/z* 195 (M^++2, 21), 193 (M^+, 93), 178 (100); HRMS calcd for $C_{10}H_8ClNO$ 193.0294, found 193.0299.

2-Acetyl-6-chloro-1*H*-indole (6n):[21] Reaction of 6-chloro-2-nitrobenzaldehyde (371 mg, 2 mmol) with 1-(triphenylphosphoranylidene)-2-propanone **8b** (637 mg, 2 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 5/1) on silica gel, gave 213 mg (55%) of **6n** as a white solid: mp 154-156ºC; ^{1}H NMR (acetone-d_6, 300 MHz, 25ºC): d 9.49 (br s, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.44 (t, *J* = 0.9 Hz, 1H), 7.18 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.12 (dd, *J* = 8.7, 2.0 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (acetone-d_6, 75.4 MHz, 25ºC): d 190.5 (C), 137.6 (C), 135.9 (C), 132.1 (C), 126.0 (C), 123.9 (CH), 122.0 (CH), 112.0 (CH), 109.8 (CH), 25.8 (CH_3); EI-LRMS *m/z* 195 (M^++2, 26), 193 (M^+, 80), 178 (100); HRMS calcd for $C_{10}H_8ClNO$ 193.0294, found 193.0291.

6-Acetyl-5*H*-[1,3]dioxolo[4,5-*f*]indole (6o): Reaction of 6-nitropiperonal (390 mg, 2 mmol) with 1-(triphenylphosphoranylidene)-2-propanone **8b** (637 mg, 2 mmol) according to the typical procedure and purification by column chromatography (hexane/EtOAc, 5/1) on silica gel, gave 317 mg (78%) of **6o** as a white solid: mp 177-179ºC (lit.[20] mp 170ºC); ^{1}H NMR (acetone-d_6, 300 MHz, 25ºC): d 10.69 (br s, 1H), 7.16 (s, 1H), 7.04 (s, 1H), 6.95 (s, 1H), 5.99 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (acetone-d_6, 75.4 MHz, 25ºC): d 189.0 (C), 149.1 (C), 144.9 (C), 136.0 (C), 135.0 (C), 122.6 (C), 110.6 (CH), 101.9 (CH_2), 100.4 (CH), 92.9 (CH), 25.6 (CH_3); EI-LRMS *m/z* 203 (M^+, 100); HRMS calcd for $C_{11}H_9NO_3$ 203.0582, found 203.0585. Spectroscopic data and analytical characterization are in complete agreement with the literature.[20]

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