

Manganese-Catalyzed Allylation via Sequential C–H and C–C/C–Het Bond Activation

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Supporting Information

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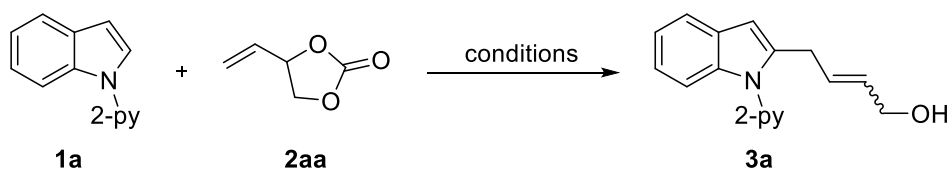
General information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in oven-dried glassware cooled down under vacuum. Reaction temperatures are reported as the temperature of the heat transfer medium surrounding the vessel unless otherwise stated. Anhydrous solvents were purchased from ROTH and stored over molecular sieves under argon. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar, ABCR, TCI Europe and used as received unless otherwise stated. *N*-2-pyridylindoles,^[1] *N*-2-pyrimidylindoles,^[2] 2-arylpyridines,^[3] 2-(prop-1-en-2-yl)pyridine,^[4] dimethyl 2-vinylcyclopropane-1,1-dicarboxylate,^[5] and meso-2,3-diazabicyclo[2.2.1]hept-5-ene-*N,N'*-diethyldicarboxylate^[6] were prepared following literature procedures. Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 366 nm). Flash chromatography was performed on Merck silica gel (40-63 mesh) by standard techniques using appropriate mixtures of *n*-pentane and ethyl acetate. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicated. Chemical shifts (δ) for ¹H and ¹³C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ¹H and ¹³C NMR spectra and the chemical shifts converted to the TMS scale (TMS: δ H = 0.00 ppm, CDCl₃: δ H = 7.26 ppm, δ C = 77.16 ppm; CD₃OD: δ H = 3.31 ppm, δ C = 49.00 ppm; DMSO-*d*₆: δ H = 2.50 ppm;). Exact ESI mass spectra were recorded on a Bruker Daltonics MicroTof. Mass Calibration was carried out directly before the measurement of the sample using clusters of sodium formate. Infrared spectra were recorded neat on a Shimadzu FTIR-8400S. The wave numbers (ν) of recorded IR-signals are quoted in cm⁻¹.

Experimental section

1) Optimization of the reaction conditions.

Table S1 | Optimization of the reaction conditions.^[a]



Entry	Cat. (10 mol%)	Additive (20 mol%)	Temp. / °C	Solvent	Yield of 3a (%)
1	[Mn ₂ (CO) ₁₀]	-	80	Et ₂ O	41
2	[Mn ₂ (CO) ₁₀]	-	80	THF	17
3	[Mn ₂ (CO) ₁₀]	-	80	Hexane	26
4	[Mn ₂ (CO) ₁₀]	-	80	DMF	79
5	[MnBr(CO) ₅]	-	80	Et ₂ O	13
6	[MnBr(CO) ₅]	Cy ₂ NH	80	Et ₂ O	72
7	[MnBr(CO) ₅]	NaOAc	80	Et ₂ O	84
8	[MnBr(CO) ₅]	NaOAc	80	DMF	55
9 ^[b]	[MnBr(CO) ₅]	NaOAc	90	Et ₂ O	90
10 ^[b]	[MnBr(CO) ₅]	NaOAc	90	neat	92
11 ^[b]	[Mn ₂ (CO) ₁₀]	NaOAc	90	neat	90
12	Cp [*] Mn(CO) ₃	NaOAc	90	Et ₂ O	0
13	Mn(OAc) ₂ ·4H ₂ O	NaOAc	90	Et ₂ O	0
14	-	NaOAc	90	Et ₂ O	0

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.2 mmol), **2aa** (0.3 mmol), catalyst precursor (10 mol%), additive (20 mol%) in solvent (1.0 mL) for 10 h, isolated yields. [b] 5 h.

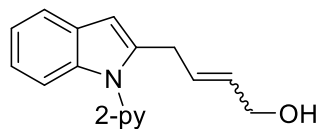
2) Procedure and analytical data of compounds 3-5.

2.1) Procedure and analytical data of compounds 3.

General procedure: In a 10 mL dry Schlenk tube with a stirring bar, *N*-2-pyridylindole (**1**) (0.20 mmol), [MnBr(CO)₅] (10 mol%, 5.5 mg) and NaOAc (20 mol%, 3.3 mg) were added under air. Then the reaction vessel was evacuated and filled with argon for three times; Afterwards, vinyl-1,3-dioxolan-2-one (**2aa**) (0.30 mmol) and Et₂O (1 mL, anhydrous, no solvent was added under neat condition) were added under an argon atmosphere. The tube was sealed and the mixture was stirred at 90 °C for the determined time. Then, the volatiles were removed and the

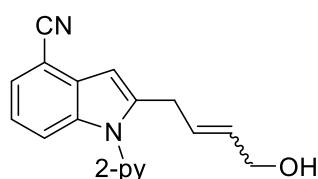
analytically pure product was obtained by flash chromatography (silica; gradient of pentane/EtOAc).

(E/Z)-4-(1-(pyridin-2-yl)-1H-indol-2-yl)but-2-en-1-ol^[7]



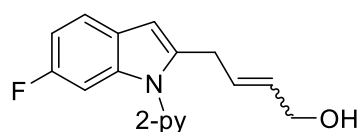
Following the general procedure, product **3a** was isolated in 89% yield. ¹H NMR (300 MHz, CDCl₃) δ 8.55 (ddd, *J* = 4.9, 1.9, 0.8 Hz, 1H), 7.85 – 7.71 (m, 1H), 7.52 – 7.44 (m, 1H), 7.35 – 7.30 (m, 1H), 7.27 – 7.19 (m, 2H), 7.09 – 6.94 (m, 2H), 6.51 – 6.20 (m, 1H), 5.71 – 5.23 (m, 2H), 3.99 (d, *J* = 5.1 Hz, 0.25 H), 3.86 (dd, *J* = 5.7, 1.1 Hz, 1.75 H), 3.62 – 3.45 (m, 2H), 1.96 (br, 1H). ¹³C NMR (75 MHz, CDCl₃) δ *Major isomer*: 151.40, 149.63, 139.04, 138.44, 137.42, 131.28, 128.65, 128.56, 122.25, 122.01, 121.24, 120.84, 120.19, 110.20, 103.29, 63.26, 30.72. *Minor isomer*: 151.34, 149.70, 139.34, 138.57, 130.42, 128.40, 122.03, 120.89, 110.14, 103.02, 58.33, 26.22. *Five peaks are missing probably due to overlap.* HRMS: *m/z* (ESI) calcd for C₁₇H₁₆N₂NaO [M+Na]⁺ 287,1160, found 287,1155.

(E/Z)-2-(4-hydroxybut-2-en-1-yl)-1-(pyridin-2-yl)-1H-indole-4-carbonitrile



Following the general procedure, product **3b** was isolated in 75% yield. ¹H NMR (300 MHz, CDCl₃) δ 8.73 – 8.42 (m, 1H), 7.97 – 7.67 (m, 1H), 7.49 – 7.24 (m, 4H), 7.15 – 6.96 (m, 1H), 6.67 – 6.49 (m, 1H), 5.76 – 5.34 (m, 2H), 4.04 (d, *J* = 6.0 Hz, 0.37 H), 3.95 (dd, *J* = 5.6, 1.3 Hz, 1.63 H), 3.59 (d, *J* = 6.7 Hz, 0.38 H), 3.54 (d, *J* = 6.5 Hz, 1.63 H), 1.68 (br, 1H). ¹³C NMR (75 MHz, CDCl₃) δ *Major isomer*: ¹³C NMR (75 MHz, CDCl₃) δ 150.36, 149.99, 142.40, 138.86, 137.17, 132.27, 130.14, 127.29, 125.89, 123.20, 121.68, 121.40, 118.83, 115.02, 102.36, 101.87, 63.17, 30.71. *Minor isomer*: ¹³C NMR (75 MHz, CDCl₃) δ 150.31, 150.07, 142.61, 138.98, 131.24, 125.93, 123.22, 121.72, 118.79, 114.93, 102.41, 101.63, 58.38, 26.25. *Four peaks are missing probably due to overlap.* HRMS: *m/z* (ESI) calcd for C₁₈H₁₅N₃NaO [M+Na]⁺ 312,1113, found 312,1107.

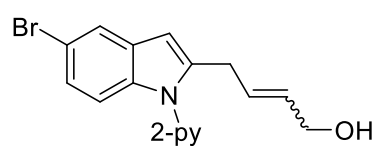
(E/Z)-4-(6-fluoro-1-(pyridin-2-yl)-1H-indol-2-yl)but-2-en-1-ol



Following the general procedure, product **3c** was isolated in 91% yield. ¹H NMR (400 MHz, CDCl₃) δ = 8.71 – 8.61 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.94 – 7.85 (m, 1H), 7.46 (dd, *J* = 8.6,

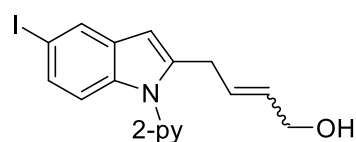
5.4 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.37 – 7.31 (m, 1H), 7.07 – 6.99 (m, 1H), 6.89 (ddd, $J = 9.5, 8.6, 2.3$ Hz, 1H), 6.44 – 6.38 (m, 1H), 5.79 – 5.44 (m, 2H), 4.10 (d, $J = 5.4$ Hz, 0.26H), 3.98 (dd, $J = 5.7, 1.3$ Hz, 1.74H), 3.62 (d, $J = 5.9$ Hz, 0.27H), 3.59 (d, $J = 6.6$ Hz, 1.74H), 1.85 (br, 1H); **^{13}C NMR (101 MHz, CDCl_3)** Major isomer: $\delta = 159.98$ (d, $J = 237.5$ Hz), 151.09, 149.74, 139.43 (d, $J = 3.8$ Hz), 138.65, 137.45 (d, $J = 12.0$ Hz), 131.44, 128.38, 124.90, 122.54, 121.01, 120.77 (d, $J = 9.9$ Hz), 109.23 (d, $J = 24.2$ Hz), 103.14, 97.19 (d, $J = 27.2$ Hz), 63.19, 30.70; Minor isomer: $\delta = 151.03, 149.83, 138.78, 130.57, 128.15, 124.89, 120.80$ (d, $J = 9.9$ Hz), 109.27 (d, $J = 24.0$ Hz), 102.85, 97.13 (d, $J = 27.3$ Hz), 58.31, 26.22. Two peaks are missing probably due to overlap, three peaks probably have too low intensities due to C-F coupling. **^{19}F NMR (282 MHz, CDCl_3)** Major isomer: $\delta = -120.86$ (td, $J = 9.8, 5.4$ Hz); Minor isomer: $\delta = -120.79$; **HRMS** m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{OFNa}$ 305.1061, found 305.1061; **ATR-IR** ν (cm^{-1}) 3333, 3082, 3063, 3013, 2905, 2862, 2357, 1616, 1586, 1570, 1559, 1470, 1439, 1385, 1354, 1296, 1273, 1207, 1180, 1138, 1096, 1049, 972, 937, 833, 810, 779, 679, 656.

(*E/Z*)-4-(5-Bromo-1-(pyridin-2-yl)-1*H*-indol-2-yl)but-2-en-1-ol



Following the general procedure, product **3d** was isolated in 89% yield. **^1H NMR (400 MHz, CDCl_3)** $\delta = 8.54 - 8.59$ (m, 1H), 7.87 – 7.77 (m, 1H), 7.63 – 7.57 (m, 1H), 7.35 – 7.29 (m, 1H), 7.27 (ddd, $J = 7.5, 4.9, 1.0$ Hz, 1H), 7.15 – 7.07 (m, 2H), 6.33 – 6.28 (m, 1H), 5.69 – 5.36 (m, 2H), 4.01 (d, $J = 5.7$ Hz, 0.33H), 3.90 (dd, $J = 5.7, 1.3$ Hz, 1.76H), 3.55 (d, $J = 6.7$ Hz, 0.34H), 3.52 (d, $J = 6.6$ Hz, 1.76H), 1.56 (br, 1H); **^{13}C NMR (101 MHz, CDCl_3)** Major isomer: $\delta = 151.01, 149.80, 140.38, 138.62, 136.15, 131.61, 130.26, 128.21, 124.76, 122.69, 122.62, 121.17, 113.97, 111.75, 102.69, 63.28, 30.71$; Minor isomer: $\delta = 150.95, 149.87, 140.66, 138.76, 130.69, 130.28, 128.06, 124.79, 122.72, 122.63, 121.19, 114.02, 111.68, 102.41, 58.40, 26.23$. One peak is missing probably due to overlap. **HRMS** m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{OBrNa}$ 365.0260, found 365.0269; **ATR-IR** ν (cm^{-1}) 3310, 3013, 2859, 1586, 1574, 1470, 1439, 1381, 1339, 1273, 1207, 1150, 1092, 1049, 972, 864, 779, 745, 733.

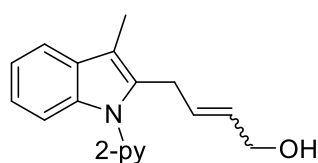
(*E/Z*)-4-(5-iodo-1-(pyridin-2-yl)-1*H*-indol-2-yl)but-2-en-1-ol



Following the general procedure, product **3e** was isolated in 91% yield. **^1H NMR (300 MHz, CDCl_3)** $\delta = 8.60 - 8.48$ (m, 1H),

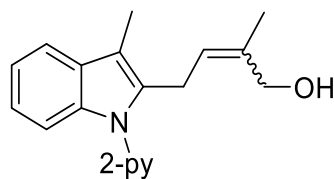
7.89 – 7.72 (m, 2H), 7.33 – 7.21 (m, 3H), 7.02 – 6.93 (m, 1H), 6.31 – 6.21 (m, 1H), 5.70 – 5.14 (m, 2H), 3.97 (d, $J = 5.5$ Hz, 0.3 H), 3.86 (dd, $J = 5.6, 1.2$ Hz, 1.7 H), 3.63 – 3.35 (m, 2H), 2.39 (br, 1H); **^{13}C NMR (75 MHz, CDCl_3)** Major isomer: δ 150.87, 149.73, 140.04, 138.65, 136.61, 131.63, 131.00, 130.24, 128.90, 128.01, 122.65, 121.20, 112.25, 102.35, 84.32, 63.13, 30.59; Minor isomer: ^{13}C NMR (75 MHz, CDCl_3) δ 150.81, 149.81, 140.31, 138.78, 130.74, 130.27, 128.93, 127.84, 112.18, 102.07, 84.36, 58.28, 26.12. Four peaks are missing probably due to overlap. **HRMS** m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{NaO}$ 413,0127, found 413,0121.

(*E/Z*)-4-(3-methyl-1-(pyridin-2-yl)-1*H*-indol-2-yl)but-2-en-1-ol



Following the general procedure, product **3f** was isolated in 97% yield. **^1H NMR (300 MHz, CDCl_3)** δ 8.58 – 8.49 (m, 1H), 7.82 – 7.77 (m, 1H), 7.52 – 7.42 (m, 1H), 7.36 – 7.28 (m, 1H), 7.27 – 7.18 (m, 2H), 7.12 – 7.01 (m, 2H), 5.56 – 5.15 (m, 2H), 3.88 (d, $J = 5.7$ Hz, 0.31H), 3.78 (dd, $J = 5.8, 1.3$ Hz, 1.68H), 3.60 (d, $J = 5.9$ Hz, 0.32H), 3.55 (dd, $J = 6.1, 1.4$ Hz, 1.69H), 2.25 (s, 0.47H), 2.23 (s, 2.48H), 1.45 (br, 1H); **^{13}C NMR (75 MHz, CDCl_3)** Major isomer: δ = 151.76, 149.56, 138.33, 136.65, 133.89, 130.24, 129.43, 129.05, 122.18, 121.93, 121.19, 120.38, 118.48, 110.82, 110.08, 63.28, 27.91, 8.89; Minor isomer: δ = 149.64, 138.50, 134.59, 129.48, 129.15, 122.21, 121.32, 120.46, 110.48, 109.98, 58.23, 23.93, 8.91. Five peaks are missing due to overlap. **HRMS** m/z (ESI): calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{OH}$ 279.1492, found 279.1494; **ATR-IR** ν (cm^{-1}) 3310, 3013, 2916, 2859, 1586, 1566, 1470, 1458, 1435, 1362, 1316, 1285, 1223, 1150, 1088, 995, 968, 779, 737.

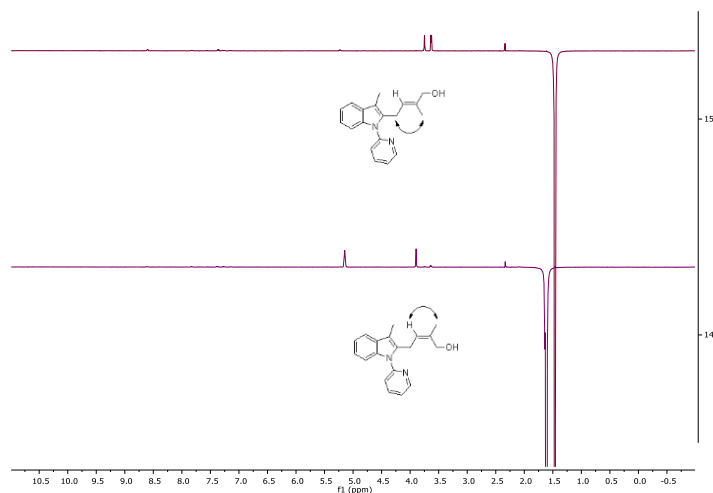
(*E/Z*)-2-methyl-4-(3-methyl-1-(pyridin-2-yl)-1*H*-indol-2-yl)but-2-en-1-ol



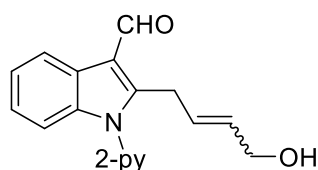
Following the general procedure, 2-methyl-2-vinyloxirane (0.6 mmol) was used instead of **2aa**, product **3g** was isolated in 69% yield. **^1H NMR (300 MHz, CDCl_3)** δ 8.49 (t, $J = 4.3$ Hz, 1H), 7.77 – 7.65 (m, 1H), 7.49 – 7.38 (m, 1H), 7.25 (t, $J = 7.4$ Hz, 1H), 7.21 – 7.10 (m, 2H), 7.09 – 6.98 (m, 2H), 5.11 (t, $J = 6.7$ Hz, 0.5H), 5.02 (t, $J = 6.9$ Hz, 0.6H), 3.77 (s, 1.1H), 3.62 (s, 0.9H), 3.57 – 3.43 (m, 2H), 2.22 (s, 3H), 2.07 (s, 1H), 1.49 (s, 1.8H), 1.34 (s, 1.3H); **^{13}C NMR (75 MHz, CDCl_3)** Major isomer: δ 151.73, 149.51, 138.41, 136.60, 135.27, 135.25, 129.48, 124.34, 122.02, 121.90, 121.38, 120.36, 118.34, 110.07, 109.93, 61.05, 23.87, 21.21, 8.87, Two peaks are missing due to overlap; Minor isomer: δ 149.58, 138.39, 136.70, 135.48, 129.42, 122.62, 121.97, 121.41,

120.28, 110.03, 109.87, 68.28, 23.94, 13.55, 8.88; Four peaks are missing due to overlap; **HRMS**: m/z (ESI) calcd for $C_{19}H_{20}N_2NaO$ $[M+Na]^+$ 315,1473, found 315,1468.

Determination of structure was achieved with TOCSY and NOE-Experiments

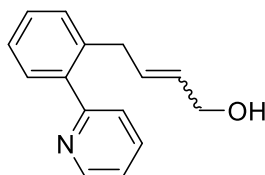


(*E/Z*)-2-(4-hydroxybut-2-en-1-yl)-1-(pyridin-2-yl)-1*H*-indole-3-carbaldehyde



Following the general procedure, product **3h** was isolated in 93% yield. **1H NMR (400 MHz, $CDCl_3$)** δ 10.22 (s, 0.24 H), 10.19 (s, 0.78 H), 8.67 – 8.57 (m, 1H), 8.24 (dt, J = 6.8, 0.9 Hz, 0.76H), 8.19 (dt, J = 6.8, 0.9 Hz, 0.24 H), 7.95 – 7.82 (m, 1H), 7.42 – 7.32 (m, 2H), 7.26 – 7.06 (m, 3H), 5.61 – 5.41 (m, 1H), 5.38 – 5.20 (m, 1H), 3.94 – 3.85 (m, 1H), 3.85 – 3.73 (m, 3H), 2.08 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** Major isomer: δ 185.32, 150.14, 149.70, 148.83, 139.01, 137.24, 132.12, 126.93, 125.68, 124.14, 124.02, 123.64, 122.20, 121.34, 115.70, 110.61, 62.79, 27.73; Minor isomer: δ 150.27, 149.65, 148.86, 139.14, 137.15, 130.74, 126.86, 126.06, 124.09, 122.26, 120.72, 115.30, 110.67, 58.09, 24.09. Three peaks are missing due to overlap. **HRMS** m/z (ESI): calcd. for $C_{18}H_{16}N_2NaO_2$ 315,1109, found 315,1104.

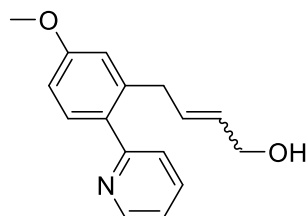
(*E/Z*)-4-(2-(pyridin-2-yl)phenyl)but-2-en-1-ol^[7]



Following the general procedure, product **3i** was isolated in 71% yield. **1H NMR (400 MHz, $CDCl_3$)** δ 8.64 – 8.47 (m, 1H), 7.73 – 7.58 (m, 1H), 7.36 – 7.10 (m, 6H), 5.66 – 5.55 (m, 0.9 H), 5.53 – 5.46 (m, 0.3 H), 5.38 – 5.29 (m, 0.9 H), 3.93 (d, J = 5.3 Hz, 0.3 H), 3.87 (dd, J = 5.9, 1.3 Hz, 1.8 H), 3.46 – 3.42 (m, 0.3 H), 3.38 (d, J = 6.6 Hz, 1.8 H), 1.91 (br, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** Major isomer: δ 159.93, 149.17, 140.43, 137.89, 136.37, 131.51, 130.29, 130.16, 129.96,

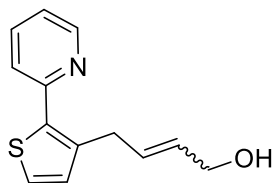
128.63, 126.47, 124.30, 121.94, 63.45, 36.08; *Minor isomer*: δ 160.07, 149.07, 140.17, 138.38, 136.65, 131.35, 130.09, 129.85, 129.20, 128.78, 126.40, 124.49, 121.98, 58.14, 31.22.

(E/Z)-4-(5-methoxy-2-(pyridin-2-yl)phenyl)but-2-en-1-ol



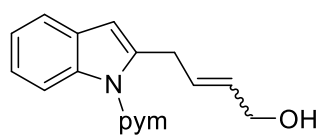
Following the general procedure, product **3j** was isolated in 81% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.65 – 8.50 (m, 1H), 7.70 – 7.57 (m, 1H), 7.29 – 7.04 (m, 3H), 6.82 – 6.69 (m, 2H), 5.68 – 5.55 (m, 0.87 H), 5.55 – 5.45 (m, 0.32 H), 5.43 – 5.26 (m, 0.85 H), 3.94 (d, J = 3.8 Hz, 0.34 H), 3.88 (d, J = 5.2 Hz, 1.73 H), 3.75 (s, 3H), 3.44 (d, J = 5.3 Hz, 0.32 H), 3.38 (d, J = 6.5 Hz, 1.69 H), 2.02 (br, 1H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) *Major isomer*: δ 159.74, 159.64, 149.10, 139.53, 133.20, 133.20, 131.30, 131.25, 130.47, 124.32, 121.58, 115.76, 111.56, 63.40, 55.39, 36.28; *Minor isomer*: δ $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 159.85, 159.80, 148.99, 140.02, 136.60, 131.43, 131.15, 129.43, 124.51, 121.61, 115.42, 111.56, 58.08, 31.37. Two peaks are missing due to overlap. **HRMS** m/z (ESI): calcd. for $\text{C}_{16}\text{H}_{17}\text{NNaO}_2$ 278,1157, found 278,1151;

(E/Z)- 4-(2-(pyridin-2-yl)thiophen-3-yl)but-2-en-1-ol^[7]



Following the general procedure, product **3k** was isolated in 70% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.71 – 8.29 (m, 1H), 7.68 – 7.56 m, 1H), 7.49 – 7.37 (m, 1H), 7.27 – 7.20 (m, 1H), 7.15 – 6.99 (m, 1H), 6.92 (d, J = 5.1 Hz, 0.18 H), 6.88 (d, J = 5.1 Hz, 0.82 H), 5.91 – 5.76 (m, 0.83 H), 5.71 – 5.65 (m, 0.34 H), 5.65 – 5.51 (m, 0.83 H), 4.18 (d, J = 5.3 Hz, 0.36 H), 4.09 – 3.95 (m, 1.70 H), 3.67 (d, J = 5.6 Hz, 0.37 H), 3.63 – 3.50 (m, 1.71 H), 1.70 (br, 1H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) *Major isomer*: δ 153.20, 149.72, 138.51, 137.54, 136.66, 131.02, 130.66, 130.48, 126.00, 122.01, 121.72, 63.49, 32.34; *Minor isomer*: δ $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 153.34, 149.54, 138.43, 136.90, 130.87, 130.64, 129.37, 125.91, 122.82, 121.82, 58.20, 27.81. One peak is missing due to overlap.

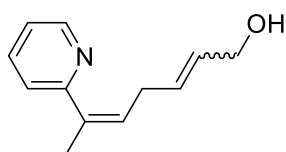
(E/Z)- 4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)but-2-en-1-ol^[7]



Following the general procedure, product **3l** was isolated in 79% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.68 (d, J = 4.8 Hz, 2H), 8.21 – 8.09 (m, 1H), 7.50 – 7.39 (m, 1H), 7.19 – 7.06 (m, 2H), 7.04 (t, J

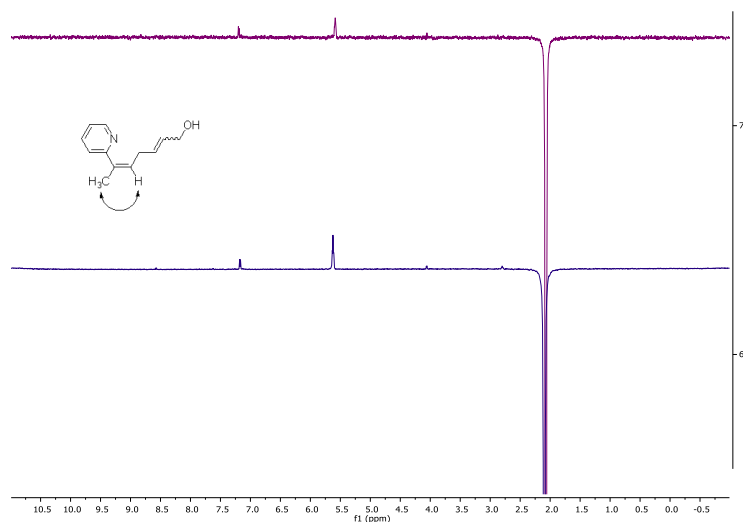
= 4.8 Hz, 1H), 6.44 – 6.34 (m, 1H), 5.84 – 5.48 (m, 2H), 4.15 (d, J = 5.3 Hz, 0.39 H), 3.93 (dd, J = 5.7, 0.87 Hz, 1.69 H), 3.90 – 3.81 (m, 2.08 H), 1.48 (br, 1H); **^{13}C NMR (75 MHz, CDCl_3)** Major isomer: δ 158.25, 139.73, 137.13, 131.12, 129.61, 129.25, 122.84, 121.96, 119.95, 117.27, 113.81, 106.56, 63.47, 32.57. Two peaks are missing due to overlap. Minor isomer: δ 158.20, 139.79, 137.16, 130.29, 129.18, 122.89, 122.02, 117.23, 113.97, 106.40, 58.67, 28.23; Four peaks are missing due to overlap.

2-(*E/Z*)-5-(*Z*)-6-(pyridin-2-yl)hepta-2,5-dien-1-ol

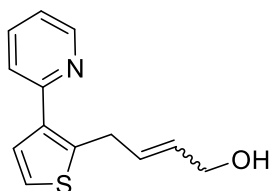


Following the general procedure, product **3m** was isolated in 75% yield. **^1H NMR (400 MHz, CDCl_3)** δ 8.52 (d, J = 3.9 Hz, 1H), 7.66 – 7.52 (m, 1H), 7.18 – 6.98 (m, 2H), 5.74 – 5.43 (m, 3H), 4.13 – 3.90 (m, 2H), 2.81 (t, J = 7.5 Hz, 0.34H), 2.74 (t, J = 3.94 Hz, 1.66H), 2.38 (br, 1H), 2.05 (s, 2.35H), 2.02 (s, 0.48H); **^{13}C NMR (101 MHz, CDCl_3)** Major isomer: δ 159.69, 149.26, 136.82, 136.16, 130.97, 129.78, 127.27, 123.13, 121.76, 63.53, 31.91, 23.90; Minor isomer: δ ^{13}C NMR (101 MHz, CDCl_3) δ 159.74, 149.00, 136.50, 135.58, 130.63, 129.21, 127.92, 121.88, 57.75, 27.80, 24.09. One peak is missing due to overlap. **HRMS** m/z (ESI): calcd. for $\text{C}_{12}\text{H}_{15}\text{NNaO}$ 212,1051, found 212,1046.

Determination of structure was achieved with TOCSY and NOE-Experiments



(*E/Z*)-4-(3-(pyridin-2-yl)thiophen-2-yl)but-2-en-1-ol



Following the general procedure, product **3n** was isolated in 65% yield.

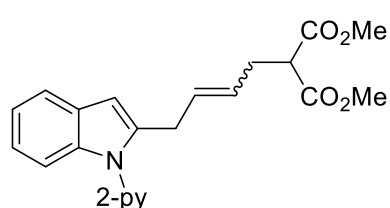
^1H NMR (300 MHz, CDCl_3) δ = 8.58 (d, J = 4.0 Hz, 1H), 7.70 – 7.57

(m, 1H), 7.42 – 7.33 (m, 1H), 7.21 (t, $J = 5.8$ Hz, 1H), 7.16 – 7.08 (m, 2H), 5.90 – 5.59 (m, 2H), 4.16 (s, 0.31H), 4.02 (s, 1.69H), 3.87 (d, $J = 6.1$ Hz, 0.30H), 3.79 (d, $J = 6.2$ Hz, 1.69H), 1.59 (s, 1H); **^{13}C NMR (101 MHz, CDCl_3)** Major isomer: $\delta = 155.15, 149.53, 141.28, 137.39, 136.52, 131.06, 130.65, 128.88, 122.89, 122.80, 121.53, 63.42, 31.79$; Minor isomer: $\delta = 155.20, 149.32, 141.95, 136.83, 136.79, 130.97, 129.90, 128.76, 123.20, 122.85, 121.63, 58.12, 27.21$; **HRMS** m/z (ESI): calcd. for $\text{C}_{13}\text{H}_{13}\text{NOSNa}$ 254.0610, found 254.0613; **ATR-IR** ν (cm^{-1}) 3275, 3063, 3013, 2893, 2855, 1586, 1566, 1535, 1466, 1439, 1420, 1373, 1339, 1277, 1231, 1150, 1092, 991, 968, 945, 856, 791, 741, 718, 679, 648.

2.2) Procedure and analytical data of compounds 4.

General procedure: In a 10 mL dry Schlenk tube with a stirring bar, *N*-2-pyridylindole (**1**) (0.20 mmol), $[\text{Mn}_2(\text{CO})_{10}]$ (10 mol%, 7.8 mg) were added under air. Then the reaction vessel was evacuated and filled with argon for three times; Afterwards, 2-vinylcyclopropane-1,1-dicarboxylate (**2ba**) (0.30 mmol) and DMF (0.2 mL, anhydrous, no solvent was added under neat condition) were added under an argon atmosphere. The tube was sealed and the mixture was stirred at 90 °C for the determined time. Then, the volatiles were removed and the analytically pure product was obtained by flash chromatography (silica; gradient of pentane/EtOAc).

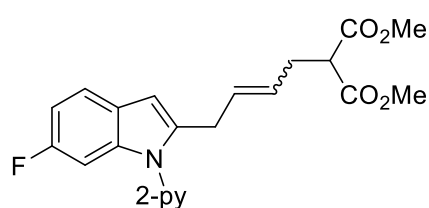
(*E/Z*)-dimethyl 2-(4-(1-(pyridin-2-yl)-1*H*-indol-2-yl)but-2-en-1-yl)malonate^[8]



Following the general procedure, $[\text{MnBr}(\text{CO})_5]$ (10 mol%) and NaOAc (20 mol%) were used to replace $\text{Mn}_2(\text{CO})_{10}$, product **4a** was isolated in 75% yield. **^1H NMR (400 MHz, CDCl_3)** δ 8.69 – 8.43 (m, 1H), 7.85 – 7.73 (m, 1H), 7.53 – 7.46 (m, 1H), 7.37 (d, $J = 8.0$ Hz, 0.35 H), 7.34 (d, $J = 8.0$ Hz, 0.73 H), 7.28 – 7.20 (m, 2H), 7.11 – 7.00 (m, 2H), 6.35 (s, 0.25 H), 6.33 (s, 0.66 H), 5.62 – 5.49 (m, 1H), 5.38 – 5.20 (m, 1H), 3.62 (s, 6H), 3.57 (d, $J = 7.3$ Hz, 0.62 H), 3.48 (d, $J = 6.7$ Hz, 1.4 H), 3.32 – 3.22 (m, 1H), 2.54 (t, $J = 8.0$ Hz, 0.55 H), 2.46 (t, $J = 7.7$ Hz, 1.42 H); **^{13}C NMR (101 MHz, CDCl_3)** Major isomer: δ 169.37, 151.42, 149.64, 139.39, 138.35, 137.37, 129.86, 128.61, 127.75, 122.12, 121.92, 121.12, 120.78, 120.14, 110.20, 103.08, 52.60, 51.75, 31.79, 31.06. Two peaks are missing due to overlap. Minor isomer: δ 169.39, 149.79, 139.43, 138.45, 137.42, 129.08, 126.49, 122.14, 102.91, 52.66, 51.63,

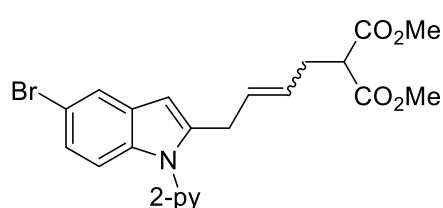
26.79, 26.05. Nine peaks are missing due to overlap.

(E/Z)-dimethyl 2-(4-(6-fluoro-1-(pyridin-2-yl)-1H-indol-2-yl)but-2-en-1-yl)malonate



Following the general procedure, product **4b** was isolated in 87% yield. **¹H NMR (400 MHz, CDCl₃)** δ 8.70 – 8.60 (m, 1H), 7.96 – 7.83 (m, 1H), 7.50 – 7.29 (m, 3H), 7.04 (dd, *J* = 10.1, 2.3 Hz, 1H), 6.88 (td, *J* = 9.1, 2.4 Hz, 1H), 6.39 (s, 0.31H), 6.37 (s, 0.66H), 5.67 – 5.54 (m, 1H), 5.46 – 5.27 (m, 1H), 3.70 (s, 6H), 3.61 (d, *J* = 7.3 Hz, 0.67H), 3.52 (d, *J* = 6.6 Hz, 1.45H), 3.40 – 3.28 (m, 1H), 2.61 (t, *J* = 7.6 Hz, 0.61H), 2.54 (t, *J* = 7.3 Hz, 1.39H). **¹³C NMR (101 MHz, CDCl₃)** Major isomer δ 169.35, 159.96 (d, *J* = 237.2 Hz), 151.11, 149.77, 139.76 (d, *J* = 3.9 Hz), 138.57, 137.38 (d, *J* = 12.2 Hz), 129.67, 127.93, 124.95, 122.42, 120.89, 120.70 (d, *J* = 9.9 Hz), 109.18 (d, *J* = 24.2 Hz), 102.94, 97.20 (d, *J* = 27.1 Hz), 52.63, 51.73, 31.77, 31.06 Two peaks are missing due to overlap. Minor isomer δ 169.38, 149.91, 139.80 (d, *J* = 4.2 Hz), 138.68, 137.44 (d, *J* = 12.2 Hz), 128.87, 126.67, 122.45, 120.90, 102.74, 52.69, 51.59, 26.79, 26.05. Eight Peaks are missing due to C-F coupling and overlap; **¹⁹F NMR (282 MHz, CDCl₃)** Major isomer: δ -121.01 (td, *J* = 9.8, 5.6 Hz); Minor isomer: δ -121.02; **HRMS** *m/z* (ESI): calcd. for C₂₂H₂₁N₂O₄FN_a 419.1378, found 419.1375; **ATR-IR** *v* (cm⁻¹) 3005, 2955, 1748, 1732, 1620, 1559, 1470, 1435, 1385, 1350, 1273, 1231, 1204, 1150, 1107, 1049, 1018, 980, 833, 810, 779, 748.

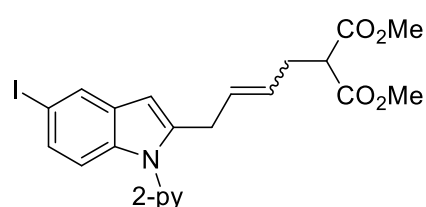
(E/Z)-dimethyl 2-(4-(5-bromo-1-(pyridin-2-yl)-1H-indol-2-yl)but-2-en-1-yl)malonate^[8]



Following the general procedure, product **4c** was isolated in 63% yield. **¹H NMR (400 MHz, CDCl₃)** δ 8.69 – 8.59 (m, 1H), 7.95 – 7.85 (m, 1H), 7.67 (t, *J* = 1.2 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.19 (d, *J* = 1.3 Hz, 2H), 6.36 (s, 0.26H), 6.34 (s, 0.69H), 5.68 – 5.55 (m, 1H), 5.46 – 5.27 (m, 1H), 3.70 (s, 4.07 H), 3.70 (s, 1.8 H), 3.62 (d, *J* = 7.3 Hz, 0.58H), 3.52 (d, *J* = 6.9 Hz, 1.50H), 3.39 – 3.30 (m, 1H), 2.61 (td, *J* = 7.6, 1.5 Hz, 0.59H), 2.54 (td, *J* = 7.4, 1.2 Hz, 1.48H); **¹³C NMR (101 MHz, CDCl₃)** δ Major isomer 169.34, 150.98, 149.78, 140.73, 138.56, 136.09, 130.29, 129.41, 128.15, 124.66, 122.62, 122.52, 121.09, 113.92, 111.75, 102.45, 52.65, 51.70, 31.77, 31.02 Two peaks are missing due to overlap. Minor isomer δ 169.37, 149.92, 140.78, 138.66, 136.15, 130.31, 128.60, 126.88, 122.54,

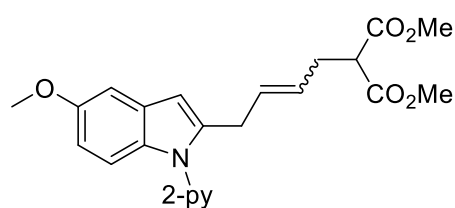
121.10, 111.73, 102.27, 52.71, 51.55, 26.80, 26.01. *Six Peaks are missing due to overlap.* **HRMS** m/z (ESI): calcd. for $C_{22}H_{21}N_2O_4BrNa$ 479.0577, found 479.0576; **ATR-IR** ν (cm^{-1}) 3005, 2951, 1748, 1732, 1586, 1543, 1435, 1385, 1339, 1273, 1231, 1204, 1150, 1049, 1015, 972, 864, 783, 733.

(E/Z)-dimethyl 2-(4-(5-iodo-1-(pyridin-2-yl)-1H-indol-2-yl)but-2-en-1-yl)malonate^[8]



Following the general procedure, product **4d** was isolated in 52% yield. **¹H NMR (400 MHz, CDCl₃)** δ 8.62 – 8.54 (m, 1H), 7.88 – 7.77 (m, 2H), 7.34 – 7.25 (m, 3H), 7.02 (d, J = 8.6 Hz, 1H), 6.27 (s, 0.27H), 6.25 (s, 0.58H), 5.63 – 5.46 (m, 1H), 5.41 – 5.19 (m, 1H), 3.63 (s, 4.23H), 3.62 (s, 1.71H), 3.54 (d, J = 7.3 Hz, 0.63H), 3.45 (d, J = 6.4 Hz, 1.30H), 3.33 – 3.23 (m, 1H), 2.53 (t, J = 7.5 Hz, 0.59H), 2.47 (t, J = 7.2 Hz, 1.34H); **¹³C NMR (101 MHz, CDCl₃)** *Major isomer* δ 169.33, 150.93, 149.78, 140.38, 138.55, 136.58, 131.08, 130.20, 129.41, 128.89, 128.14, 122.52, 121.09, 112.26, 102.16, 84.27, 52.65, 51.70, 31.77, 30.95. *Two peaks are missing due to overlap.* *Minor isomer* δ 169.36, 149.92, 140.44, 138.65, 136.64, 128.61, 126.88, 122.54, 112.24, 101.98, 52.71, 51.55, 26.79, 25.95. *Eight Peaks are missing due to overlap;* **HRMS** m/z (ESI): calcd. for $C_{22}H_{21}IN_2NaO_4$ 527,0444, found 527,0438;

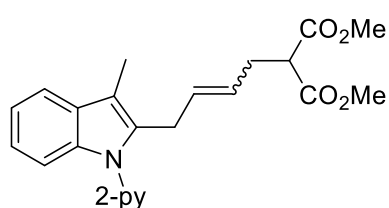
(E/Z)-dimethyl 2-(4-(5-methoxy-1-(pyridin-2-yl)-1H-indol-2-yl)but-2-en-1-yl)malonate^[8]



Following the general procedure, product **4e** was isolated in 90% yield. **¹H NMR (400 MHz, CDCl₃)** δ 8.61 – 8.48 (m, 1H), 7.86 – 7.70 (m, 1H), 7.34 (d, J = 8.0 Hz, 0.27H), 7.30 (d, J = 8.0 Hz, 0.77H), 7.23 – 7.13 (m, 2H), 6.95 (d, J = 2.4 Hz, 1H), 6.69 (dd, J = 8.9, 2.5 Hz, 1H), 6.28 (s, 0.25H), 6.25 (s, 0.70H), 5.60 – 5.46 (m, 1H), 5.36 – 5.20 (m, 1H), 3.76 (s, 3H), 3.62 (s, 6H), 3.56 (d, J = 7.3 Hz, 0.57H), 3.47 (d, J = 6.6 Hz, 1.46H), 3.22 – 3.21 (m, 1H), 2.55 (t, J = 7.2 Hz, 0.53H), 2.46 (t, J = 7.2 Hz, 1.43H); **¹³C NMR (101 MHz, CDCl₃)** *Major isomer* δ 169.34, 154.86, 151.48, 149.54, 139.89, 138.31, 132.43, 129.88, 129.14, 127.67, 121.88, 120.75, 111.40, 111.01, 102.98, 102.30, 55.90, 52.58, 51.72, 31.76, 31.13. *Two peak is missing due to overlap.* *Minor isomer* δ 169.36, 149.68, 139.95, 138.41, 132.47, 129.10, 126.39, 121.90, 110.99, 102.80, 52.64, 51.59, 26.76, 26.13. *Nine*

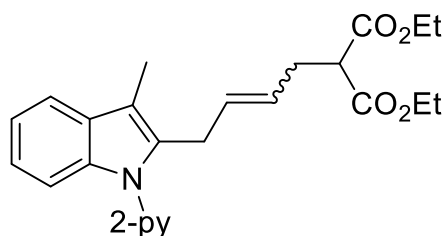
peaks are missing due to overlap.

(E/Z)-dimethyl 2-(4-(3-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)but-2-en-1-yl)malonate^[8]



Following the general procedure, $[\text{MnBr}(\text{CO})_5]$ (10 mol%) and NaOAc (20 mol%) were used to replace $\text{Mn}_2(\text{CO})_{10}$, product **4f** was isolated in 89% yield. **¹H NMR (400 MHz, CDCl_3)** δ 8.58 – 8.49 (m, 1H), 7.81 – 7.72 (m, 1H), 7.49 – 7.42 (m, 1H), 7.30 (t, J = 8.3 Hz, 1H), 7.28 – 7.15 (m, 2H), 7.10 – 7.01 (m, 2H), 5.46 – 5.35 (m, 0.64H), 5.33 – 5.22 (m, 0.37H), 5.14 – 4.98 (m, 1H), 3.66 – 3.60 (m, 2.91H), 3.56 (s, 3.83H), 3.50 (d, J = 5.9 Hz, 1.32H), 3.22 – 3.10 (m, 1H), 2.43 (t, J = 7.4 Hz, 0.72H), 2.35 (t, J = 7.3 Hz, 1.32H), 2.25 (s, 1.08H), 2.20 (s, 2.20H); **¹³C NMR (101 MHz, CDCl_3)** Major isomer δ 169.30, 151.70, 149.51, 138.21, 136.54, 133.94, 130.27, 129.42, 126.46, 122.05, 121.77, 121.03, 120.28, 118.35, 110.69, 110.12, 52.50, 51.76, 31.71, 28.19, 8.77. Two peak is missing due to overlap. Minor isomer δ 169.36, 149.74, 138.32, 136.58, 134.76, 129.86, 129.47, 125.14, 122.06, 121.08, 120.32, 118.38, 110.37, 109.94, 52.62, 51.46, 26.74, 23.65, 8.87. Four peaks are missing due to overlap.

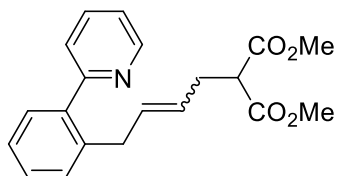
(E/Z)-diethyl 2-(4-(3-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)but-2-en-1-yl)malonate



Following the general procedure, $[\text{MnBr}(\text{CO})_5]$ (10 mol%) and NaOAc (20 mol%) were used to replace $\text{Mn}_2(\text{CO})_{10}$, product **4g** was isolated in 95% yield using diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2bb**) as the starting material. **¹H NMR (300 MHz, CDCl_3)** δ 8.58 – 8.50 (m, 1H), 7.81 – 7.71 (m, 1H), 7.51 – 7.42 (m, 1H), 7.36 – 7.14 (m, 3H), 7.09 – 7.00 (m, 2H), 5.48 – 5.34 (m, 0.7H), 5.32 – 5.20 (m, 0.3H), 5.17 – 4.97 (m, 1H), 4.18 – 3.93 (m, 4H), 3.63 (d, J = 6.7 Hz, 0.6H), 3.49 (d, J = 5.8 Hz, 1.3H), 3.19 – 3.06 (m, 1H), 2.43 (t, J = 7.4 Hz, 0.7H), 2.35 (t, J = 7.3 Hz, 1.4H), 2.25 (s, 1H), 2.20 (s, 2H), 1.17 (t, J = 7.1 Hz, 2H), 1.10 (t, J = 7.1 Hz, 4.2H); **¹³C NMR (75 MHz, CDCl_3)** Major isomer: δ 168.93, 151.68, 149.48, 138.21, 136.51, 133.94, 130.05, 129.40, 126.65, 122.01, 121.76, 121.04, 120.25, 118.32, 110.64, 110.09, 61.38, 52.05, 31.63, 28.17, 14.09, 8.77, Two peaks are missing due to overlap; Minor isomer: δ 169.00, 149.71, 138.31, 136.55, 134.81, 129.63, 129.45, 125.34, 121.07, 120.29, 118.36, 110.33, 109.93, 61.50, 51.78, 26.66, 23.66, 14.17, 8.87; Five peaks are missing due to overlap; **HRMS**: m/z (ESI)

calcd for $C_{25}H_{28}N_2NaO_4$ $[M+Na]^+$ 443,1947, found 443,1941.

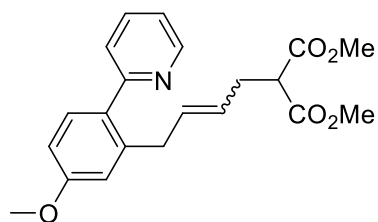
(E/Z)-dimethyl 2-(4-(2-(pyridin-2-yl)phenyl)but-2-en-1-yl)malonate^[8]



Following the general procedure, $[MnBr(CO)_5]$ (10 mol%) and NaOAc (20 mol%) were used to replace $Mn_2(CO)_{10}$, product **4h** was isolated in 57% yield. 1H NMR (300 MHz, $CDCl_3$) δ 8.67 – 8.55 (m, 1H), 7.73 – 7.62 (m, 1H), 7.33 – 7.14 (m, 6H), 5.58 –

5.41 (m, 1H), 5.29 – 5.10 (m, 1H), 3.64 (s, 1.68H), 3.61 (s, 4.27H), 3.45 (d, J = 7.3 Hz, 0.56H), 3.34 (d, J = 6.5 Hz, 1.48H), 3.31 – 3.22 (m, 1H), 2.56 – 2.41 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) Major isomer δ 169.43, 160.01, 149.31, 140.41, 138.03, 136.27, 132.73, 129.95, 129.91, 128.51, 126.57, 126.37, 124.27, 121.84, 52.64, 51.67, 36.23, 31.90. Two peaks are missing due to overlap; Minor isomer δ 160.01, 149.31, 138.42, 136.41, 131.93, 129.97, 129.77, 128.65, 126.33, 125.10, 124.31, 52.64, 51.67, 31.09, 26.79. Five Peaks are missing due to overlap; HRMS m/z (ESI): calcd. for $C_{20}H_{21}NNaO_4$ 362,1368, found 362,1363.

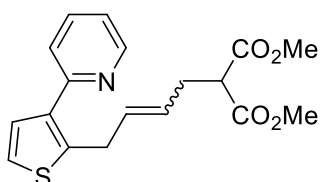
(E/Z)-dimethyl 2-(4-(5-methoxy-2-(pyridin-2-yl)phenyl)but-2-en-1-yl)malonate^[8]



Following the general procedure, product **4i** was isolated in 50% yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.51 (m, 1H), 7.70 – 7.57 (m, 1H), 7.32 – 7.21 (m, 2H), 7.14 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 6.82 – 6.64 (m, 2H), 5.60 – 5.47 (m, 1H),

5.31 – 5.14 (m, 1H), 3.77 (s, 3H), 3.64 (s, 1.07H), 3.61 (s, 4.92H), 3.46 (d, J = 7.9 Hz, 0.34H), 3.35 (d, J = 6.6 Hz, 1.62H), 3.32 – 3.23 (m, 1H), 2.57 – 2.40 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) Major isomer δ 169.43, 159.74, 159.67, 149.19, 139.69, 136.20, 133.20, 132.58, 131.25, 126.78, 124.28, 121.47, 115.47, 111.63, 55.40, 52.56, 51.89, 36.44, 31.90. Two peaks are missing due to overlap. Minor isomer δ ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.83, 149.25, 140.06, 136.34, 131.81, 131.31, 125.31, 124.32, 115.32, 111.58, 52.63, 51.67, 31.30, 26.81. Seven peaks are missing due to overlap; HRMS m/z (ESI): calcd. for $C_{21}H_{24}NO_5$ 370,1654, found 370,1649.

(E/Z)-Dimethyl-2-(4-(4-(pyridin-2-yl)thiophen-3-yl)but-2-en-1-yl)malonate



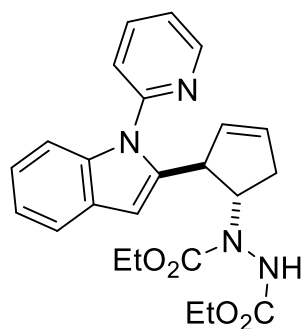
Following the general procedure, product **4j** was isolated in 53% yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.53 (m, 1H), 7.68 – 7.59 (m, 1H), 7.40 – 7.32 (m, 1H), 7.24 – 7.20 (m, 1H), 7.14 – 7.05

(m, 2H), 5.76 – 5.61 (m, 1H), 5.51 – 5.28 (m, 1H), 3.87 (dd, $J = 7.3, 1.6$ Hz, 0.50H), 3.74 (dd, $J = 6.6, 1.4$ Hz, 1.49H), 3.66 (s, 1.43H), 3.64 (s, 4.56H), 3.40 – 3.31 (t, $J = 7.6$ Hz, 1H), 2.68 (td, $J = 7.6, 1.6$ Hz, 0.50H), 2.55 (m, 1.50H); ^{13}C NMR (101 MHz, CDCl_3) Major isomer $\delta = 169.41, 155.14, 149.54, 141.68, 137.25, 136.44, 131.91, 128.84, 127.56, 122.84, 122.72, 121.45, 52.65, 51.81, 32.21, 31.81$ Two peaks are missing due to overlap, Minor isomer $\delta = 169.44, 155.23, 141.98, 137.06, 136.50, 131.14, 128.82, 126.12, 122.57, 121.44, 52.70, 51.69, 27.17, 26.90$ Four peaks are missing due to overlap; HRMS m/z (ESI): calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_4\text{SNa}$ 368.0927, found 368.0929; ATR-IR ν (cm^{-1}) 3005, 2951, 1748, 1732, 1586, 1566, 1532, 1474, 1435, 1339, 1269, 1235, 1200, 1150, 1022, 972, 856, 791, 745, 718, 702.

2.3) Procedure and analytical data of compounds 5.

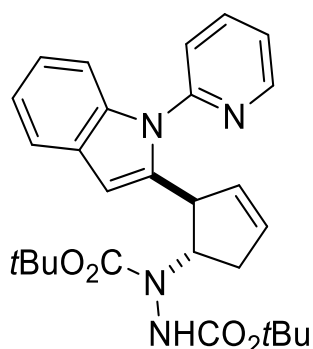
General procedure: In a 10 mL dry Schlenk tube with a stirring bar, *N*-2-pyridylindole (**1**) (0.20 mmol), $[\text{MnBr}(\text{CO})_5]$ (10 mol%, 5.5 mg) and NaOAc (20 mol%, 3.3 mg) were added under air. Then the reaction vessel was evacuated and filled with argon for three times; Afterwards, diazabicyclo (**2ca**) (0.30 mmol) and Et_2O (1 mL, anhydrous, no solvent was added under neat condition) were added under an argon atmosphere. The tube was sealed and the mixture was stirred at 90 °C for the determined time. Then, the volatiles were removed and the analytically pure product was obtained by flash chromatography (silica; gradient of pentane/EtOAc).

diethyl 1-(2-(1-(pyridin-2-yl)-1*H*-indol-2-yl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate



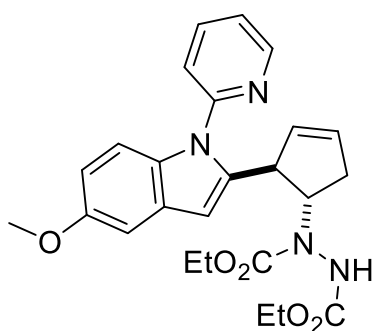
Following the general procedure, product **5a** was isolated in 83% yield. ^1H NMR (400 MHz, CD_3OD) δ 8.61 (d, $J = 3.9$ Hz, 1H), 8.02 (td, $J = 7.8, 1.9$ Hz, 1H), 7.56 (d, $J = 7.9$ Hz, 1H), 7.54 – 7.49 (m, 1H), 7.45 (dd, $J = 7.5, 5.0$ Hz, 1H), 7.20 – 7.13 (m, 1H), 7.11 – 7.03 (m, 2H), 6.51 (s, 1H), 5.80 – 5.68 (m, 1H), 5.59 (s, 1H), 5.12 (s, 1H), 4.45 – 4.27 (m, 1H), 4.21 – 3.86 (m, 4H), 2.66 (dd, $J = 17.2, 8.4$ Hz, 1H), 2.57 – 2.36 (m, 1H), 1.39 – 0.96 (m, 6H); ^{13}C NMR (101 MHz, CD_3OD) δ 157.53, 155.93, 150.98, 149.13, 141.82, 139.23, 137.91, 130.94, 129.06, 128.39, 122.82, 122.57, 121.67, 120.37, 119.81, 109.58, 101.28, 64.89, 62.11, 61.39, 46.10, 34.60, 13.49, 13.38; HRMS: m/z (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{N}_4\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 457,1852, found 457,1846. ATR-IR ν (cm^{-1}) 3279, 2982, 2931, 1748, 1701, 1589, 1469, 1454, 1435, 1142, 1230, 1211, 1126, 1057, 953, 926, 787, 741, 702, 3005.

di-tert-butyl 1-(-2-(1-(pyridin-2-yl)-1*H*-indol-2-yl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate



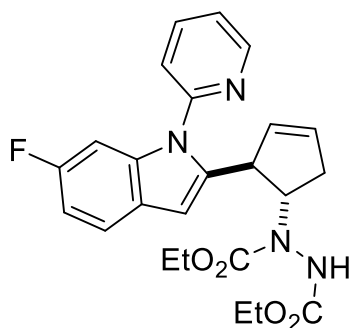
Following the general procedure, product **5b** was isolated in 70% yield using di-tert-butyl 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**2cb**) as the starting material. **¹H NMR (600 MHz, CD₃OD)** δ 8.62 (d, *J* = 5.0 Hz, 1H), 8.01 (s, 1H), 7.65 – 7.40 (m, 3H), 7.21 – 7.12 (m, 1H), 7.12 – 6.98 (m, 2H), 6.54 (s, 1H), 5.69 (s, 1H), 5.52 (s, 1H), 5.15 (s, 1H), 4.29 (s, 1H), 2.67 – 2.45 (m, 2H), 1.65 – 1.05 (m, 18H); **¹³C NMR (126 MHz, CD₃OD)** δ 157.79, 156.45, 152.42, 150.57, 150.46, 140.60, 139.32, 132.49, 130.21, 129.84, 124.23, 123.96, 122.95, 121.72, 121.11, 110.94, 102.65, 82.15, 81.63, 64.05, 47.25, 35.76, 28.61, 28.50; **HRMS**: *m/z* (ESI) calcd for C₂₈H₃₄N₄NaO₄ [M+Na]⁺ 513.2478, found 513.2472.

diethyl 1-(-2-(5-methoxy-1-(pyridin-2-yl)-1*H*-indol-2-yl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate



Following the general procedure, product **5c** was isolated in 94% yield. **¹H NMR (400 MHz, CD₃OD)** δ 8.59 (d, *J* = 3.8 Hz, 1H), 8.09 – 7.92 (m, 1H), 7.52 (s, d, *J* = 7.9 Hz, 1H), 7.43 (dd, *J* = 7.1, 5.2 Hz, 1H), 7.09 (d, *J* = 8.9 Hz, 1H), 7.04 (d, *J* = 2.3 Hz, 1H), 6.73 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.44 (s, 1H), 5.77 – 5.68 (m, 1H), 5.59 (s, 1H), 5.10 (s, 1H), 4.45 – 4.27 (m, 1H), 4.16 – 3.94 (m, 4H), 3.79 (s, 3H), 2.74 – 2.57 (m, 1H), 2.55 – 2.43 (m, 1H), 1.26 – 1.05 (m, 6H); **¹³C NMR (101 MHz, CD₃OD)** δ 158.80, 157.30, 156.29, 152.47, 150.41, 143.81, 140.56, 134.35, 132.36, 130.37, 130.12, 123.96, 123.60, 112.64, 111.72, 103.33, 102.67, 66.21, 63.47, 62.76, 56.13, 47.52, 36.03, 14.85, 14.74; **HRMS**: *m/z* (ESI) calcd for C₂₅H₂₈N₄NaO₅ [M+Na]⁺ 487.1957, found 487.1952.

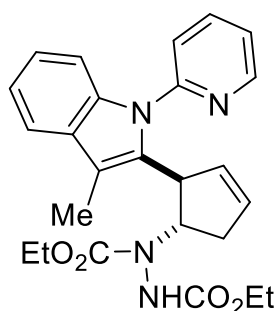
diethyl 1-(-2-(6-fluoro-1-(pyridin-2-yl)-1*H*-indol-2-yl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate



Following the general procedure, product **5d** was isolated in 81% yield. **¹H NMR (400 MHz, CD₃OD)** δ 8.63 (d, *J* = 3.7 Hz,

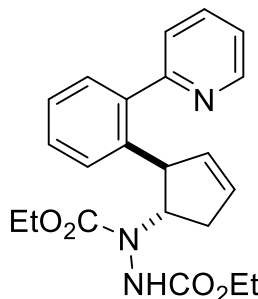
1H), 8.05 (t, $J = 7.6$ Hz, 1H), 7.56 (d, $J = 7.9$ Hz, 1H), 7.52 – 7.42 (m, 2H), 6.94 – 6.82 (m, 2H), 6.50 (s, 1H), 5.72 (dd, $J = 5.7, 2.2$ Hz, 1H), 5.58 (s, 1H), 5.10 (s, 1H), 4.32 (s, 1H), 4.18 – 3.95 (m, 4H), 2.78 – 2.57 (m, 1H), 2.56 – 2.38 (m, 1H), 1.30 – 1.12 (m, 6H); **^{13}C NMR (101 MHz, CD_3OD)** δ 161.21 (d, $J = 237.5$ Hz), 158.87, 157.28, 152.01, 150.66, 143.96, 140.77, 139.31, 139.19, 132.36, 130.57, 126.22, 124.47, 123.75, 122.03 (d, $J = 9.7$ Hz), 109.89 (d, $J = 24.3$ Hz), 102.59, 97.63 (d, $J = 27.4$ Hz), 65.25, 63.53, 62.76, 47.58, 35.96, 14.84, 14.74; **^{19}F NMR (564 MHz, CDCl_3)** δ -122.62. **HRMS:** m/z (ESI) calcd for $\text{C}_{24}\text{H}_{25}\text{FN}_4\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 475,1758, found 475,1752.

diethyl 1-(2-(3-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate



Following the general procedure, $[\text{MnBr}(\text{CO})_5]$ (20 mol%) and NaOAc (40 mol%) were used under neat condition at 100 °C for 37 h, product **5e** was isolated in 94% yield. **^1H NMR (400 MHz, CD_3OD)** δ 8.58 (s, 1H), 7.97 (td, $J = 7.8, 1.8$ Hz, 1H), 7.54 – 7.48 (m, 1H), 7.48 – 7.38 (m, 2H), 7.13 – 7.00 (m, 3H), 5.71 – 5.51 (m, 2H), 5.33 (br, 1H), 4.34 (s, 1H), 4.20 – 3.88 (m, 4H), 2.71 – 2.47 (m, 2H), 2.34 (s, 3H), 1.30 – 0.88 (m, 6H); **^{13}C NMR (126 MHz, CD_3OD)** δ 158.64, 157.60, 153.05, 150.26, 140.20, 138.63, 137.56, 132.40, 131.06, 129.81, 124.52, 124.04, 123.09, 121.18, 118.97, 111.68, 110.74, 67.27, 63.37, 62.82, 47.18, 36.30, 14.71, 14.46, 9.03; **HRMS:** m/z (ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{N}_4\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 471,2008, found 471,2003.

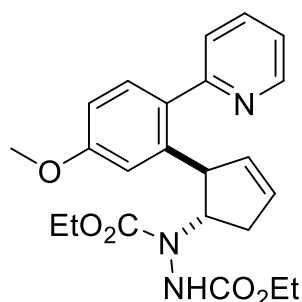
diethyl 1-(2-(2-(pyridin-2-yl)phenyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate^[9]



Following the general procedure, $[\text{MnBr}(\text{CO})_5]$ (20 mol%) and NaOAc (40 mol%) were used under neat condition at 100 °C for 37 h. product **5f** was isolated in 78% yield. The structure was determined by comparison with the reported literature.^[9] **^1H NMR (300 MHz, CD_3OD)** δ 8.78 – 8.49 (m, 1H), 7.90 (d, $J = 1.8$ Hz, 1H), 7.49 (dt, $J = 7.8, 1.1$ Hz, 1H), 7.46 – 7.16 (m, 5H), 5.78 (dd, $J = 6.0, 2.5$ Hz, 1H), 5.69 – 5.50 (m, 1H), 4.95 (s, 1H), 4.30 (s, 1H), 4.23 – 3.88 (m, 4H), 2.59 (m, 2H), 1.42 – 0.81 (m, 6H); **^{13}C NMR (75 MHz, CD_3OD)** δ 160.99, 158.58, 157.45, 149.36, 141.49, 138.69, 134.62, 131.04, 130.12, 128.95, 127.56, 126.69, 123.56,

69.99, 63.37, 62.78, 50.87, 36.14, 14.85, 14.66; **HRMS**: m/z (ESI) calcd for $C_{22}H_{25}N_3NaO_4$ $[M+Na]^+$ 418,1743, found 418,1737.

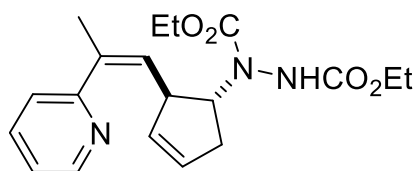
Diethyl 1-(2-(2-(5-methoxyphenyl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate^[9]



Following the general procedure, $[MnBr(CO)_5]$ (20 mol%) and NaOAc (40 mol%) were used under neat condition at 100 °C for 37 h. product **5g** was isolated in 72% yield. The structure was determined by comparison with the reported literature.^[9] **1H NMR (400 MHz, CD_3OD)** 8.78 – 8.44 (m, 1H), 7.86 (t, J = 7.3 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.41 – 7.31 (m, 1H), 7.25 (d, J = 9.0 Hz, 1H), 6.96 –

6.79 (m, 2H), 5.86 – 5.73 (m, 1H), 5.56 (s, 1H), 4.97 (s, 1H), 4.42 – 4.29 (m, 1H), 4.19 – 3.90 (m, 4H), 3.82 (s, 3H), 2.78 – 2.38 (m, 2H), 1.34 – 0.96 (m, 6H); **^{13}C NMR (101 MHz, CD_3OD)** δ 161.68, 160.84, 158.51, 157.53, 149.25, 138.66, 134.56, 134.13, 132.56, 130.29, 126.77, 123.19, 114.19, 113.11, 69.91, 63.40, 62.88, 55.73, 50.73, 36.01, 14.86, 14.64; **HRMS**: m/z (ESI) calcd for $C_{23}H_{27}N_3NaO_5$ $[M+Na]^+$ 448,1848, found 448,1843.

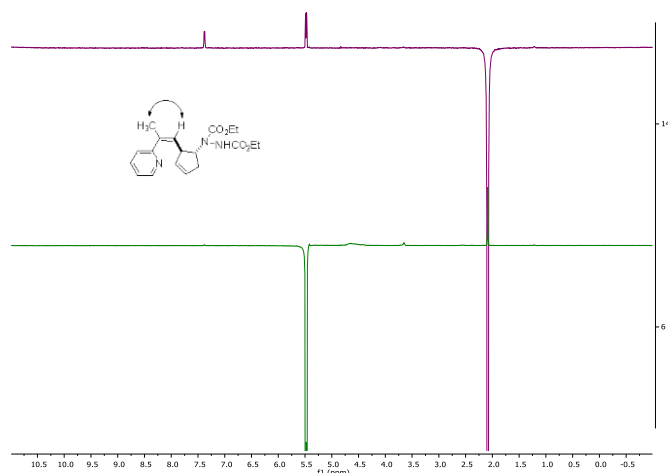
diethyl 1-(2-((Z)-2-(pyridin-2-yl)prop-1-en-1-yl)cyclopent-3-en-1-yl)hydrazine-1,2-dicarboxylate



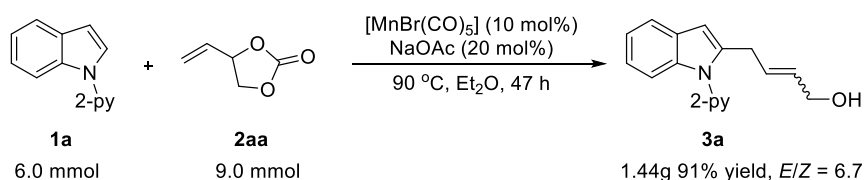
Following the general procedure, $[MnBr(CO)_5]$ (20 mol%) and NaOAc (40 mol%) were used at 100 °C for 24 h, product **5h** was isolated in 62% yield. **1H NMR (400 MHz, CD_3OD)** δ 8.53 (s, 1H), 7.80 (t, J = 7.2 Hz, 1H), 7.37 (d, J

= 7.9 Hz, 1H), 7.33 – 7.24 (m, 1H), 5.74 – 5.59 (m, 1H), 5.50 – 5.46 (m, 1H), 5.44 – 5.38 (m, 1H), 4.63 (br, 1H), 4.24 – 4.00 (m, 4H), 3.72 – 3.60 (m, 1H), 2.66 – 2.28 (m, 4H), 2.08 (d, J = 1.1 Hz, 3H), 1.28 – 1.15 (m, 6H); **^{13}C NMR (101 MHz, CD_3OD)** δ 160.65, 158.60, 157.80, 149.52, 138.52, 137.90, 133.62, 132.78, 129.93, 125.01, 123.47, 66.91, 63.48, 62.70, 36.50, 35.75, 24.45, 14.86, 14.83; **HRMS**: m/z (ESI) calcd for $C_{19}H_{25}N_3NaO_4$ $[M+Na]^+$ 382,1743, found 382,1748.

Determination of structure was achieved with TOCSY and NOE-Experiments

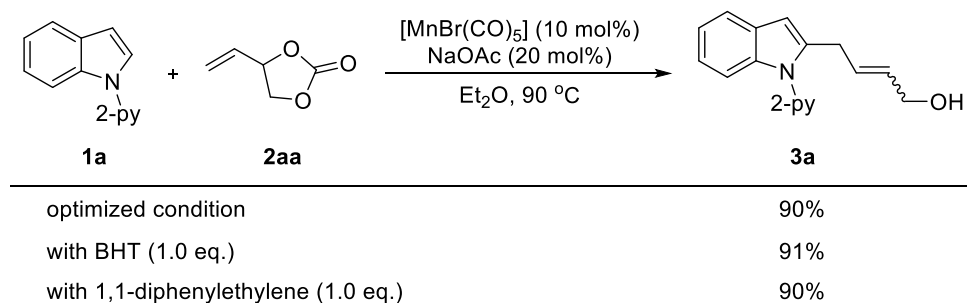


3) Gram-scale synthesis of **1a**.



General procedure: In a 100 mL dry Schlenk tube with a stirring bar, *N*-2-pyridylindole (**1a**) (6.0 mmol), $[\text{MnBr}(\text{CO})_5]$ (10 mol%, 165 mg) and NaOAc (20 mol%, 98.4 mg) were added under air. Then the reaction vessel was evacuated and filled with argon for three times; Afterwards, vinyl-1,3-dioxolan-2-one (**2aa**) (9.0 mmol) and Et_2O (20 mL, anhydrous) were added under an argon atmosphere. The tube was sealed and the mixture was stirred at 90 °C for 47 h. Then, the volatiles were removed and the analytically pure product was obtained in 91% yield (1.44 g, $E/Z = 6.7$) by flash chromatography (silica; gradient of pentane/EtOAc).

4) Radical trapping experiments.

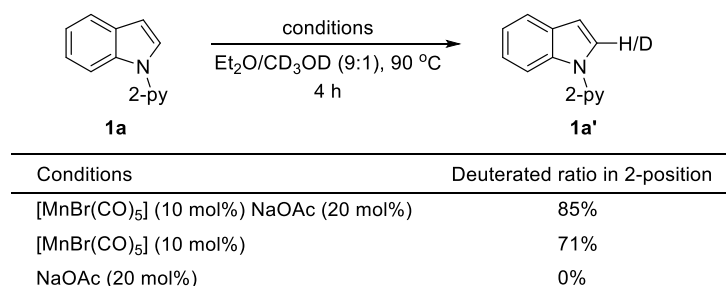


Scheme S1. Radical trapping experiments, isolated yield.

General procedure: In a 10 mL dry Schlenk tube with a stirring bar, *N*-2-pyridylindole (**1a**) (0.2

mmol), radical inhibitor (0.2 mmol), [MnBr(CO)₅] (10 mol%, 5.5 mg) and NaOAc (20 mol%, 3.2 mg) were added under air. Then the reaction vessel was evacuated and filled with argon for three times; Afterwards, vinyl-1,3-dioxolan-2-one (**2aa**) (0.3 mmol) and Et₂O (1 mL, anhydrous) were added under an argon atmosphere. The tube was sealed and the mixture was stirred at 90 °C for 5 h. Then, the volatiles were removed and the analytically pure product was obtained by flash chromatography (silica; gradient of pentane/EtOAc).

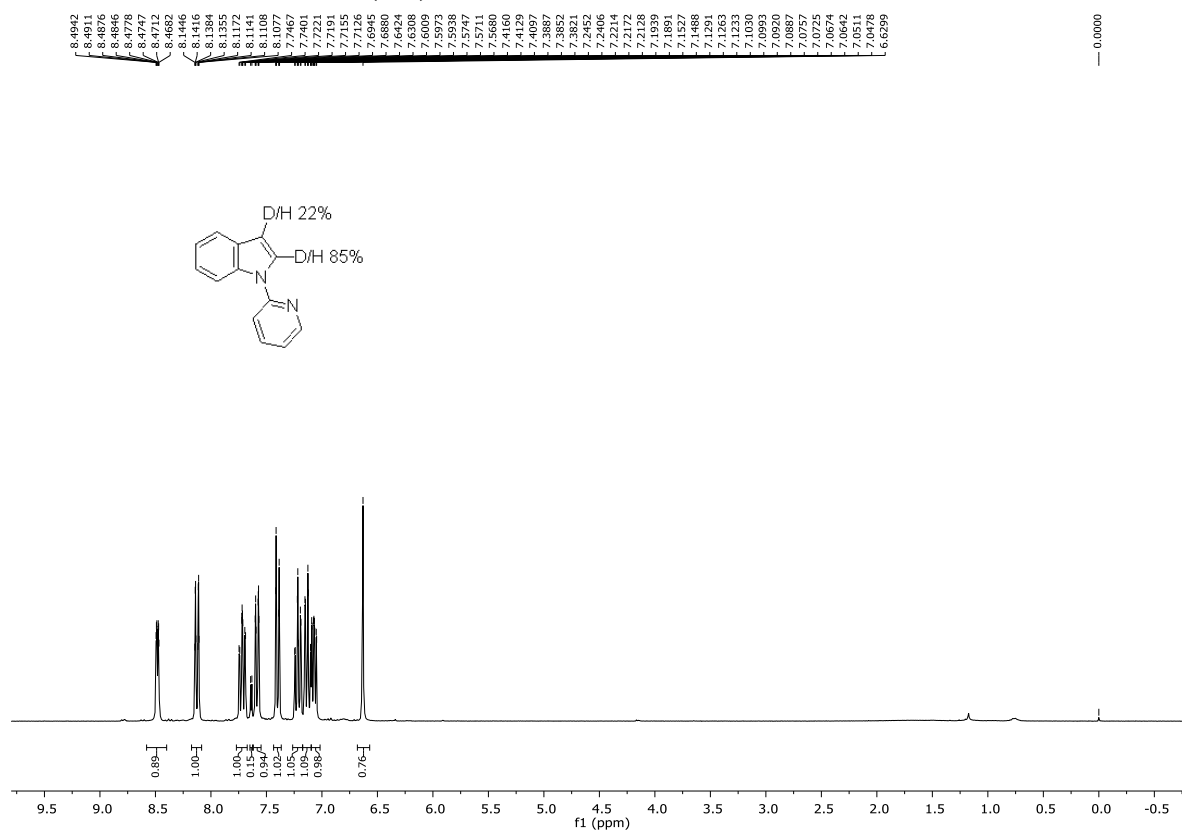
5) H/D scrambling experiments.



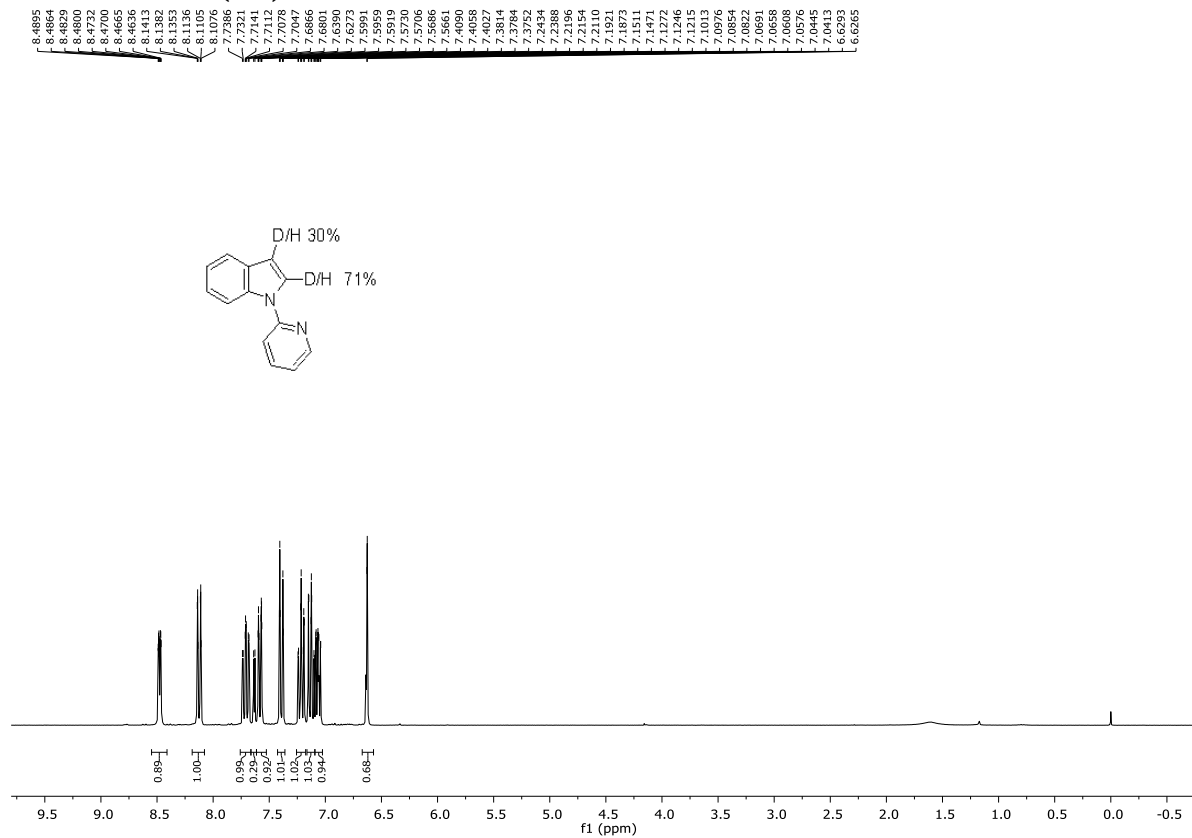
Scheme S2. H/D scrambling experiments.

General procedure: In a 10 mL dry Schlenk tube with a stirring bar, *N*-2-pyridylindole (**1a**) (0.2 mmol), [MnBr(CO)₅] (10 mol%, 5.5 mg) and/or NaOAc (20 mol%, 3.2 mg) were added under air. Then the reaction vessel was evacuated and filled with argon for three times; Afterwards, Et₂O (0.9 mL, anhydrous) and CD₃OD (0.1 mL) were added under an argon atmosphere. The tube was sealed and the mixture was stirred at 90 °C for 4 h. Then, the volatiles were removed and the analytically pure product was obtained by flash chromatography (silica; gradient of pentane/EtOAc). The H/D-ratio was determined by ¹H NMR.

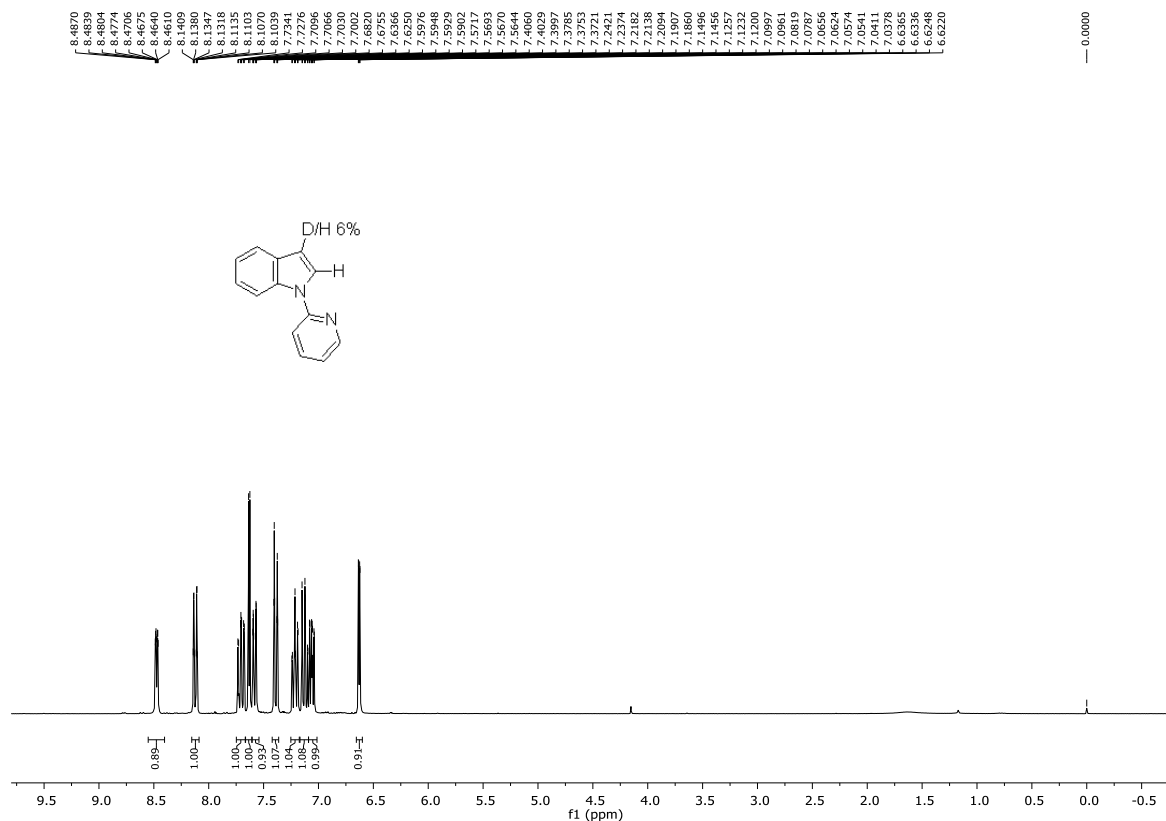
Condition: NaOAc and MnBr(CO)₅



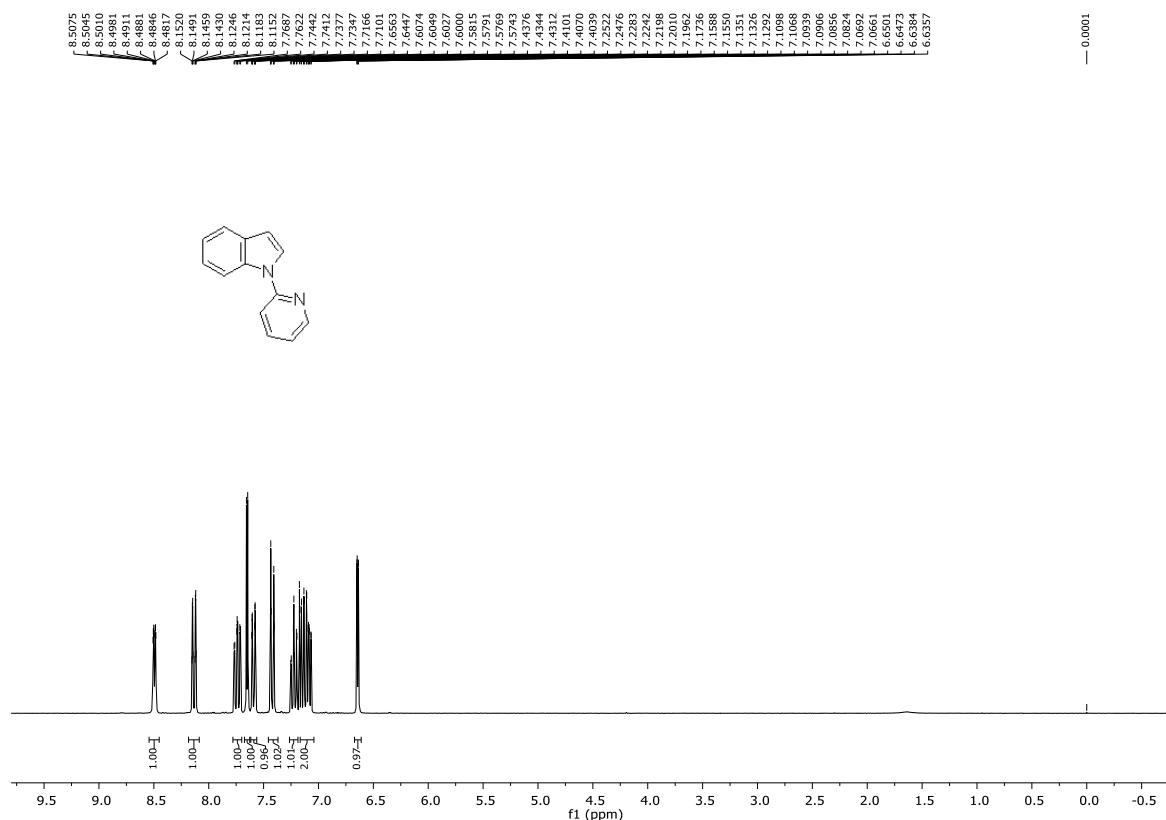
Condition: MnBr(CO)₅



Condition: NaOAc



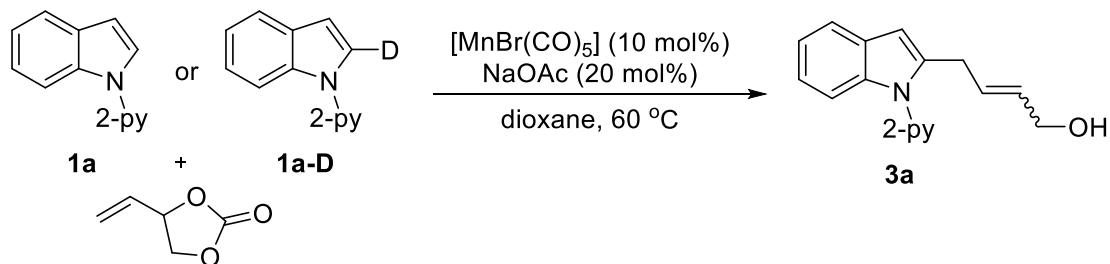
1-(pyridin-2-yl)-1H-indole



S23

6) KIE experiments.

Parallel experiments for the synthesis of allylic alcohol.

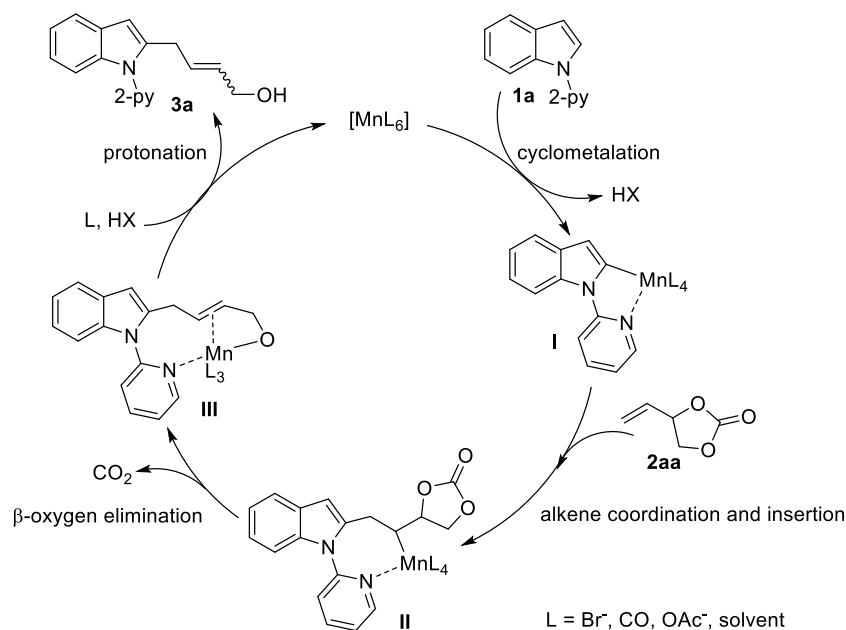


Following the general procedure 2.1, *N*-2-pyridylindole (**1a**) (0.20 mmol) or 2-deuterated *N*-2-pyridylindole (**1a-D**) (0.20 mmol), $[\text{MnBr}(\text{CO})_5]$ (10 mol%, 5.5 mg) NaOAc (20 mol%, 3.3 mg), 1,3,5-trimethoxybenzene (0.068 mmol, internal standard), vinyl-1,3-dioxolan-2-one (**2aa**) (0.30 mmol) and dioxane (2 mL, anhydrous) were added under an argon atmosphere in two different reaction tubes. The reactions were stirred at 60 °C and samples of 100 μL were taken at intervals to analyze by ^1H NMR. KIE value was measured averaging for each run. Note: The yields of **3a** are 55% and 54% respectively when **1a** or **1a-D** was submitted under the optimized condition for 5 minutes, therefore, 60 °C was used.

Reaction Time	Yield of 3a (1a was used) %	Yield of 3a (1a-D was used) %
5 min	11	10
10 min	32	30
30 min	49	48
$k_{\text{H}}/k_{\text{D}}$ (on average)	1.0	

7) Proposed mechanism.

The proposed reaction pathway is depicted in Scheme S3. The reaction starts with the base-assisted cyclomanganation of *N*-(2-pyridyl)-indole **1a**, forming a five-membered manganacycle **I**. Afterwards, coordination of vinyl-1,3-dioxolan-2-one (**2aa**) to manganacycle **I** is followed by a migratory insertion to furnish the seven-membered manganacycle **II**, which undergoes β -oxygen elimination and subsequent protonolysis to deliver the desired product **3a** and regenerate the active manganese(I) complex. Here the *anti*- β -oxygen elimination of the manganacycle **II** to afford the *trans*-adduct as a major product might be a favorable pathway.



Scheme S3. Proposed mechanism.

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NMR Spectra of Products

