Supporting Information

Manganese-Catalyzed Aerobic Dehydrogenative Cyclization toward Ring-Fused Indole Skeletons

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1. General Method

¹H NMR spectra were recorded on a JEOL JNM-LA500 spectrometer operating at 500 MHz for ¹H NMR and 125.65 MHz for ¹³C NMR. Chemical shifts were reported downfield from TMS ($\delta = 0$ ppm) for ¹H NMR. For ¹³C NMR, chemical shifts were reported in the scale relative to the solvent used as an internal reference. ESI-mass spectra were measured on a JEOL JMS-T100LC AccuTOF spectrometer (for HRMS). Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM). Indoles **1a-i** were prepared as described in this Supporting Information. Other reagents were purchased from Aldrich, TCI (Tokyo Chemical Industry Co., Ltd.), Kanto Chemical Co., Inc., and Wako Pure Chemical Industries, Ltd. and used without further purification.

2. General Procedure for Construction of Ring-Fused Indole Skeleton



1a (30 mg, 0.104 mmol), $Mn(acac)_3$ (3.7 mg, 0.0105 mmol) and xylenes (1.0 mL) were added in a flamed-dried test tube. The three-way cock was changed to $CaCl_2$ tube and the mixture was stirred at 130 °C by using heat block under air for 15 h. The mixture was directly purified by flash column chromatography (silica gel, hexane/ethyl acetate = 4:1) to afford **2a** (84% yield). All entries were performed with the same procedure except for purification process (varied eluent systems were used). Typical reaction setup is as photographed below.



3. Substrate Synthesis

dimethyl 2-(3-(1H-indol-3-yl)propyl)malonate (1a)



According to the reported procedure¹, **S2** was obtained in 41% yield (for 2 steps). .

Then, DMF (12 mL), HMPA (15 mL), sodium hydride (467 mg, 0.0195 mol) and dimethylmalonate (2.53g, 0.0192 mol) were added in a flamed-dried flask and the reaction mixture was stirred at room temperature for 90 min. Then, the reaction mixture was added in a flamed-dried flask which was filled with **S2** (3.85 g, 0.0162 mol), DMF (19 mL) and HMPA (2.0 mL). The reaction mixture was stirred at room temperature for 14 h. The reaction mixture was diluted with ethyl acetate and the organic phase was washed with water, dried over Na₂SO₄, filtered and evaporated to give crude **1a**. Crude **1a** was purified by silica gel column chromatography (hexane/ethyl acetate=4/1) to give pure **1a** in 57% yield (2.67 g) as yellow oil.

dimethyl 2-(3-(5-bromo-1H-indol-3-yl)propyl)malonate (1b) dimethyl 2-(3-(7-bromo-1H-indol-3-yl)propyl)malonate (1c) dimethyl 2-(3-(5-methoxy-1H-indol-3-yl)propyl)malonate (1d)



According to the reported procedure², **S3b**, **S3c** and **S3d** were obtained in 72%, 64% and 8% yield, respectively.

Then, **S3b** (3.41 g, 0.0134 mol), dichloromethane (13.5 mL), triphenylphosphine (5.27 g, 0.0201 mol) and *N*-bromosuccineimide (3.58 g, 0.0201 mol) were added in a flamed-dried flask and the reaction mixture was stirred at room temperature for 21 h. The organic phase was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = $10/1 \rightarrow 3/1$) to give **S4b** in 66% yield (2.81 g) as yellow oil. Using the same procedure as that for **S4b**, **S4c** and **S4d** were obtained in 36% and 50% yield, respectively.

Then, using the same procedure as that for **1a**, **1b**, **1c** and **1d** were obtained in 63%, 63% and 52% yield as yellow oil, respectively.

dimethyl 2-(3-(1-methyl-1H-indol-3-yl)propyl)malonate (1e)



S1 (5.54 g, 0.0316 mol), DCM (160 mL), TBSCl (5.72 g, 0.0380 mol) and Et_3N (6.2 mL, 0.0443 mol) were added in a flamed-dried flask and the reaction mixture was stirred at room temperature for 18.5 h. The reaction was quenched with sat. NH₄Cl aq. The organic phase was washed with brine, dried over Na₂SO₄, filtered and evaporated to give crude **S5**. Crude **S5** was purified by silica gel column chromatography (hexane/ethyl acetate=8/1) to give **S5** in 79% (7.21 g) as red oil.

S5 (2.00 g, 6.91 mmol), sodium hydride (249 mg, 10.4 mmol) and THF (23 mL) were added in a flamed-dried flask at 0 °C and the reaction mixture was stirred at room temperature for 90 min. Then, methyl iodide (560 μ L, 9.00 mmol) was added in the reaction at 0 °C and the reaction mixture was stirred at room temperature for 14.5 h. The reaction was quenched with sat. NH₄Cl aq. Products were extracted with diethylether. The combined organic layers were washed with sat. NaHCO₃ aq., dried over Na₂SO₄, filtered and evaporated to give crude **S6**. Crude **S6** was purified by silica gel column chromatography (hexane/ethyl acetae=30/1) to give **S6** in 41% yield (1.19 g) as brown oil.

S6 (1.19 g, 0.00392 mol), THF (13 mL) and 1 M TBAF in THF (7.8 mL, 0.00780 mol) were added in a flamed-dried flask at 0 °C and the reaction mixture was stirred at room temperature for 17 h. The reaction mixture was diluted with ethyl acetate and the organic phase was washed with sat. NH₄Cl aq., dried over Na₂SO₄, filtered and evaporated to give crude **S7**. Crude **S7** was purified by silica gel column chromatography (hexane/ethyl acetate=2/1) to give **S7** in 97% yield (717 mg) as yellow oil.

Using the same procedure as that for S8 was obtained in 45% yield as yellow oil.

Then, using the same procedure as that for **1a** except for the purification method from silica column chromatography to preparative thin layer chromatography, **1e** was obtained in 8% yield as yellow oil.

dimethyl 2-(2-(1H-indol-3-yl)ethyl)malonate (1f)



According to the reported procedure², **S9** was obtained in 46% yield as yellow oil.

Then, using the same procedure as that for 1a, 1f was obtained in 43% yield as yellow oil (for 2 steps).

dimethyl 2-(4-(1H-indol-3-yl)butyl)malonate (1g)



Using the same procedure as that for **1a**, **1g** was obtained in 7% yield as yellow oil (for 3 steps).

dimethyl 2-(3-(1H-indol-1-yl)propyl)malonate (1h)



According to the procedure³, **S13** was obtained in 92% yield as yellow oil.

Then, using the same procedure as that for **1a**, **1h** was obtained in 2% yield as yellow oil (for 2 steps).

dimethyl 2-(2-(1H-indol-1-yl)ethyl)malonate (1i)



According to the procedure⁴, **S15** was obtained in 88% yield as yellow oil.

Then, using the same procedure as that for 1a, 1i was obtained in 35% yield as that yellow oil.

4. Characterization of Synthetic Intermediates

3-(1H-indol-3-yl)propan-1-ol (S1)



¹H NMR (CDCl₃): $\delta = 7.83$ (1H, s), 7.73-7.48 (1H, m), 7.38-6.98 (3H, m), 6.89 (1H, s), 3.65 (2H, t, J = 6.1 Hz), 2.75 (2H, t, J = 6.1 Hz), 2.11 (1H, s); ¹³C NMR (CDCl₃): $\delta =$ 136.37, 127.39, 121.74, 121.51, 119.00, 118.79, 115.54, 111.21, 62.44, 32.84, 21.30; HRMS (ESI): m/z calcd for C₁₁H₁₃NONa [M+Na]⁺ 198.0895. Found 198.0888.

3-(3-bromopropyl)-1H-indole (S2)



¹H NMR (CDCl₃): $\delta = 7.86-7.26$ (2H, m), 7.20-6.96 (3H, m), 6.80 (1H, d, J= 2.3 Hz), 3.26 (2H, t, J = 5.8 Hz), 2.80 (2H, t, J = 6.1 Hz), 2.40-1.83 (2H, m); ¹³C NMR $(CDCl_3)$: $\delta = 136.39, 127.35, 122.10, 121.86, 119.37, 118.88, 114.60, 111.26, 33.94,$ 32.94, 23.40; HRMS (ESI): m/z calcd for C₁₁H₁₂BrNNa [M+Na]⁺ 260.0051. Found

260.0040.

3-(5-bromo-1H-indol-3-yl)propan-1-ol (S3b)

NMR spectra of the obtained product were consistent with the reported one⁵.



3-(7-bromo-1H-indol-3-yl)propan-1-ol (S3c)



¹H NMR (CDCl₃): $\delta = 7.56$ (1H, d, J = 8.2 Hz), 7.34 (1H, d, J = 8.2 Hz), 7.07 (1H, s), 6.99 (1H, t, *J* = 8.2 Hz), 3.73 (2H, t, *J* = 6.1 Hz), 2.85 (2H, t, *J* = 8.2 Hz), 1.99 (2H, m); ¹³C NMR (CDCl₃): δ = 135.10, 128.81, 124.33, 122.09, 120.41, 118.22, 117.26, 104.84, 62.47, 32.90, 21.53; HRMS (ESI): m/z calcd for C₁₁H₁₂BrNONa [M+Na]⁺ 276.0000.

Found 276.0013.

3-(5-methoxy-1H-indol-3-yl)propan-1-ol (S3d)

NMR spectra of the obtained product were consistent with the reported one⁵.





5-bromo-3-(3-bromopropyl)-1H-indole (S4b)



¹H NMR (CDCl₃): $\delta = 7.22$ (1H, s), 7.27-7.24 (2H, m), 7.05 (1H, s), 3.45 (2H, t, J =6.3 Hz), 2.90 (2H, t, J = 8.2 Hz), 2.22 (2H, m); ¹³C NMR (CDCl₃): $\delta = 135.07$, 128.59, 124.44, 122.43, 120.59, 118.17, 115.95, 104.88, 33.70, 32.85, 23.54; HRMS (ESI): m/z calcd for C₁₁H₁₁Br₂NNa [M+Na]⁺ 337.9156 (51%), 339.9136

(100%). Found 339.9141.

7-bromo-3-(3-bromopropyl)-1H-indole (S4c)



¹H NMR (CDCl₃): δ = 7.56 (1H, d, *J* = 8.2 Hz), 7.35 (1H, d, *J* = 7.1 Hz), 7.10 (1H, s), 7.00 (1H, t, *J* = 8.2 Hz), 3.43 (2H, t, *J* = 7.3 Hz), 2.93 (2H, t, *J* = 7.2 Hz), 2.24 (2H, m); ¹³C NMR (CDCl₃): δ = 135.07, 128.59, 124.44, 122.43, 120.59, 118.16, 115.95, 104.88, 33.70, 32.85, 23.54; HRMS (ESI): m/z calcd for C₁₁H₁₁Br₂NNa [M+Na]⁺ 337.9156

(51%), 339.9136 (100%). Found 339.9130.

3-(3-bromopropyl)-5-methoxy-1*H*-indole (S4d)



¹H NMR (CDCl₃): δ = 7.24 (1H, m), 7.05-7.02 (2H, m), 6.88 (1H, d, *J* = 6.2 Hz), 3.86 (3H, s), 3.45 (2H, t, *J* = 6.2 Hz), 2.91 (2H, t, *J* = 7.1 Hz), 2.23 (2H, m); ¹³C NMR (CDCl₃): δ = 154.04, 131.62, 127.86, 122.71, 114.46, 112.29, 111.99, 100.84, 56.09, 34.00, 32.96, 23.40; HRMS (ESI): m/z calcd for C₁₂H₁₄BrNONa

 $[M+Na]^+$ 290.0157. Found 290.0166.

3-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-1H-indole (S5)



¹H NMR (CDCl₃): δ = 7.61 (1H, d, *J* = 8.1 Hz), 7.35 (1H, d, *J* = 8.5 Hz), 7.18 (1H, t, *J* = 7.2 Hz), 7.11 (1H, t, *J* = 8.2 Hz), 6.99 (1H, s), 3.70 (2H, t, *J* = 6.3 Hz), 2.82 (2H, t, *J* = 8.2 Hz), 1.94 (2H, m), 0.92 (9H, s), 0.065 (6H, s); ¹³C NMR (CDCl₃): δ = 136.43, 127.67, 121.89, 121.31, 119.13, 119.05, 116.35, 111.16, 62.91, 33.29, 26.13, 21.41,

18.49, -5.09; HRMS (ESI): m/z calcd for $C_{17}H_{27}NOSiNa [M+Na]^+ 312.1760$. Found 312.1750.

3-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-1-methyl-1*H*-indole (S6)



¹H NMR (CDCl₃): δ = 7.60 (1H, d, *J* = 7.1 Hz), 7.30 (1H, d, *J* = 8.5 Hz), 7.19 (1H, t, *J* = 7.1 Hz), 7.07 (1H, t, *J* = 6.7 Hz), 6.83 (1H, s), 3.74 (3H, s), 3.69 (2H, t, *J* = 6.2 Hz), 2.80 (2H, t, *J* = 7.6 Hz), 1.92 (2H, m), 0.92 (9H, s), 0.064 (6H, s); ¹³C NMR (CDCl₃): δ = 137.17, 128.10, 126.17, 121.52, 119.20, 118.59, 115.02, 109.17, 62.89,

33.60, 32.59, 26.14, 21.37, 18.49, -5.08; HRMS (ESI): m/z calcd for $C_{18}H_{19}NOSiNa [M+Na]^+$ 326.1916. Found 326.1925.

3-(1-methyl-1H-indol-3-yl)propan-1-ol (S7)



¹H NMR (CDCl₃): δ = 7.60 (1H, d, *J* = 8.2 Hz), 7.28 (1H, d, *J* = 8.2 Hz), 7.22 (1H, t, *J* = 7.1 Hz), 7.10 (1H, t, *J* = 7.1 Hz), 6.85 (1H, s), 3.72 (2H, t, *J* = 6.4 Hz), 2.85 (2H, t, *J* = 7.2 Hz), 1.98 (2H, m); ¹³C NMR (CDCl₃): δ = 137.11, 127.90, 126.23, 121.53, 119.02, 118.63, 114.47, 109.21, 62.54, 33.18, 32.53, 21.30; HRMS (ESI): m/z calcd for

 $C_{12}H_{15}NONa \ [M+Na]^+ 212.1051. Found 212.1048.$

3-(3-bromopropyl)-1-methyl-1H-indole (S8)



¹H NMR (CDCl₃): δ = 7.60 (1H, d, *J* = 8.1 Hz), 7.29 (1H, d, *J* = 8.1 Hz), 7.23 (1H, d, *J* = 6.7 Hz), 7.11 (1H, d, *J* = 6.7 Hz), 6.89 (1H, s), 3.75 (3H, s), 3.44 (2H, t, *J* = 5.8 Hz), 2.93 (2H, t, *J* = 6.7 Hz), 2.23 (2H, m); ¹³C NMR (CDCl₃): δ = 137.21, 127.84, 126.76, 121.70, 119.02, 118.83, 113.12, 109.35, 33.97, 33.24, 32.73, 23.37; HRMS (ESI): m/z

calcd for $C_{12}H_{14}BrNNa [M+Na]^+ 274.0207$. Found 274.0198.

2-(1H-indol-3-yl)ethan-1-ol (S9)



¹H NMR (CDCl₃): δ = 7.63 (1H, d, *J* = 8.1 Hz), 7.36 (1H, d, *J* = 8.1 Hz), 7.20 (1H, t, *J* = 6.2 Hz), 7.13 (1H, t, *J* = 6.1 Hz), 7.05 (1H, s), 4.35 (2H, t, *J* = 6.3 Hz), 3.10 (2H, t, *J* = 6.3 Hz); ¹³C NMR (CDCl₃): δ = 136.45, 127.41, 122.71, 122.10, 119.39, 118.81, 112.02, 111.36, 62.59, 28.69; HRMS (ESI): m/z calcd for C₁₀H₁₁NONa [M+Na]⁺ 184.0738.

Found 184.0732.

3-(2-bromoethyl)-1H-indole (S10)



¹H NMR (CDCl₃): δ = 7.59 (1H, d, *J* = 8.1 Hz), 7.38 (1H, d, *J* = 8.1 Hz), 7.21 (1H, t, *J* = 7.0 Hz), 7.14 (1H, t, *J* = 7.0 Hz), 7.10 (1H, s), 3.64 (2H, t, *J* = 8.2 Hz), 3.34 (2H, t, *J* = 8.2 Hz); ¹³C NMR (CDCl₃): δ = 136.17, 127.00, 122.36, 122.30, 119.67, 118.56, 113.49, 111.39, 33.06, 29.37; HRMS (ESI): m/z calcd for C₁₀H₁₀BrNNa [M+Na]⁺ 245.9894.

Found 245.9894.

4-(1H-indol-3-yl)butan-1-ol (S11)



¹H NMR (CDCl₃): δ = 7.61 (1 H, d, *J* = 8.1 Hz), 7.35 (1H, d, *J* = 8.1 Hz), 7.18 (1H, t, *J* = 6.3 Hz), 7.11 (1H, t, *J* = 6.3 Hz), 6.99 (1H, s), 3.68 (2H, t, *J* = 5.6 Hz), 2.81 (2H, t, *J* = 6.8 Hz), 1.84-1.64 (4H, m); ¹³C NMR (CDCl₃): δ = 136.29, 127.37, 121.52, 121.46, 118.79, 118.73, 115.92, 62.50, 32.36, 26.19, 24.76; HRMS (ESI): m/z calcd for

C₁₂H₁₅NONa [M+Na]⁺ 212.1051. Found 212.1044.

3-(4-bromobutyl)-1H-indole (S12)



¹H NMR (CDCl₃): δ = 7.59 (1H, d, *J* = 8.1 Hz), 7.35 (1H, d, *J* = 8.1 Hz), 7.19 (1H, t, *J* = 6.8 Hz), 7.11 (1H, t, *J* = 6.8 Hz), 6.99 (1H, s), 3.45 (2H, t, *J* = 5.1 Hz), 2.80 (2H, t, *J* = 7.1 Hz), 1.99-1.85 (4H, m); ¹³C NMR (CDCl₃): δ = 136.44, 127.55, 122.09, 121.34, 119.32, 119.00, 116, 21, 111.22, 34.04, 32.69, 28.72, 24.40; HRMS (ESI): m/z calcd for

 $C_{12}H_{14}BrNNa [M+Na]^+ 274.0207$. Found 274.0194.

2-(1H-indol-1-yl)ethan-1-ol (S13)

NMR spectra of the obtained product were consistent with the reported one³.



1-(2-bromoethyl)-1H-indole (S14)

NMR spectra of the obtained product were consistent with the reported one⁶.

1-(3-bromopropyl)-1H-indole (S15)



NMR spectra of the obtained product were consistent with the reported one⁴.

5. Characterization of Starting and Target Compounds

dimethyl 2-(3-(1H-indol-3-yl)propyl)malonate (1a)



¹H NMR (CDCl₃): $\delta = 7.57$ (1H, d, J = 8.0 Hz), 7.35 (1H, d, J = 8.0 Hz), 7.18 (1H, t, J = 8.2 Hz), 7.11 (1H, t, J = 8.2 Hz), 6.99 (1H, s), 3.71 (6H, s), 3.41 (1H, t, J = 3.2 Hz), 2.79 (2H, t, J = 6.7 Hz), 2.02 (2H, t, J = 6.7 Hz), 1.75 (2H, m); ¹³C NMR (CDCl₃): $\delta = 170.06$, 136.45, 127.46, 121.95, 121.45, 119.20, 118.88,

115.79, 111.21, 52.57, 51.70, 28.79, 27.80, 24.84; HRMS (ESI): m/z calcd for $C_{16}H_{19}NO_4Na$ [M+Na]⁺ 312.1212. Found 312.1225.

dimethyl 2-(3-(5-bromo-1H-indol-3-yl)propyl)malonate (1b)



¹H NMR (CDCl₃): δ = 7.68 (1H, s), 7.24-7.21 (2H, m), 6.99 (1H, s), 3.73 (6H, s), 3.41 (1H, t, *J* = 7.2 Hz), 2.74 (2H, t, *J* = 7.2 Hz), 2.00 (2H, m), 1.73 (2H, m); ¹³C NMR (CDCl₃): δ = 170.06, 135.05, 129.22, 124.70, 122.78, 121.45, 115.42, 112.70, 112.43, 52.63, 51.61, 28.68, 27.65, 24.63; HRMS

(ESI): m/z calcd for $C_{16}H_{18}BrNO_4Na [M+Na]^+$ 390.0317. Found 390.0307.

dimethyl 2-(3-(7-bromo-1H-indol-3-yl)propyl)malonate (1c)



¹H NMR (CDCl₃): δ = 7.52 (1H, d, *J* = 8.6 Hz), 7.34 (1H, d, *J* = 8.2 Hz), 7.05 (1H, s), 6.99 (1H, dd, *J* = 8.6 Hz), 3.72 (6H, s), 3.40 (1H, t, *J* = 7.3 Hz), 2.77 (2H, t, *J* = 7.2 Hz), 2.01 (2H, m), 1.73 (2H, m); ¹³C NMR (CDCl₃): δ = 169.96, 135.08, 128.70, 124.30, 122.10, 120.40, 118.15, 117.10, 104.81, 52.59, 51.63,

28.69, 27.73, 25.96; HRMS (ESI): m/z calcd for $C_{16}H_{18}BrNO_4Na [M+Na]^+$ 390.0317. Found 390.0312.

dimethyl 2-(3-(5-methoxy-1H-indol-3-yl)propyl)malonate (1d)



¹H NMR (CDCl₃): δ = 7.25 (1H, m), 7.00 (1H, d, *J* = 20 Hz), 6.84 (1H, d, *J* = 6.1 Hz), 3.87 (3H, s), 3.72 (6H, s), 3.42 (1H, t, *J* = 8.1 Hz), 2.76 (2H, t, *J* = 7.2 Hz), 2.03 (2H, m), 1.74 (2H, m); ¹³C NMR (CDCl₃): δ = 170.06, 153.95, 131.63, 127.84, 122.29, 115.64, 112.18, 111.92, 100.84, 56.07,

52.60, 51.72, 28.81, 27.69, 24.88; HRMS (ESI): m/z calcd for $C_{17}H_{21}NO_4Na$ [M+Na]⁺ 342.1317. Found 342.1327.

dimethyl 2-(3-(1-methyl-1H-indol-3-yl)propyl)malonate (1e)



¹H NMR (CDCl₃): $\delta = 7.60$ (1H, d, J = 7.1 Hz), 7.30 (1H, d, J = 8.5 Hz), 7.19 (1H, t, J = 7.1 Hz), 7.07 (1H, t, J = 6.7 Hz), 6.83 (1H, s), 3.74 (3H, s), 3.69 (2H, t, J = 6.2 Hz), 2.80 (2H, t, J = 7.6 Hz), 1.92 (2H, m), 0.92 (9H, s), 0.064 (6H, s) ; ¹³C NMR (CDCl₃): $\delta = 170.00$, 137.12, 127.84, 126.26, 121.53, 118.63, 114.35,

109.22, 52.52, 51.70, 32.63, 28.78, 28.05, 24.77; HRMS (ESI): m/z calcd for $C_{17}H_{21}NO_4Na$ $[M+Na]^+$ 326.1368. Found 326.1355.

dimethyl 2-(2-(1H-indol-3-yl)ethyl)malonate (1f)



¹H NMR (CDCl₃): $\delta = 7.60$ (1H, d, J = 8.0 Hz), 7.35 (1H, d, J = 8.0 Hz), 7.18 (1H, t, J = 7.0 Hz), 7.13 (1H, t, J = 7.0 Hz), 7.01 (1H, s), 3.72 (6H, s), 3.46 (1H, t, J = 8.3 Hz), 2.82 (2H, t, J = 8.3 Hz), 2.33 (2H, q, J = 7.1 Hz); ¹³C NMR (CDCl₃): $\delta = 170.07$, 136.41, 127.25, 121.25, 119.95, 118.77, 114.34, 111.25,

52.53, 52.42, 51.20, 29.31, 22.86; HRMS (ESI): m/z calcd for $C_{15}H_{17}NO_4Na$ [M+Na]⁺ 298.1055. Found 298.1068.

dimethyl 2-(4-(1H-indol-3-yl)butyl)malonate (1g)



¹H NMR (CDCl₃): δ = 7.58 (1H, d, *J* = 8.2 Hz), 7.35 (1H, d, *J* = 8.1 Hz), 7.17 (1H, t, *J* = 8.1 Hz), 7.10 (1H, t, *J* = 8.1 Hz), 6.97 (1H, s), 3.72 (6H, s), 3.36 (1H, t, *J* = 7.4 Hz), 2.76 (2H, t, *J* = 7.2 Hz), 1.97 (2H, m), 1.74 (2H, m), 1.42 (2H, m); ¹³C NMR (CDCl₃): δ = 170.11, 136.45, 127.58, 121.93, 121.28, 119.17, 118.49,

116.49, 111.17, 52.57, 51.80, 29.73, 28.84, 27.30, 24.90; HRMS (ESI): m/z calcd for $C_{17}H_{21}NO_4Na$ $[M+Na]^+$ 326.1368. Found 326.1369.

dimethyl 2-(2-(1H-indol-1-yl)ethyl)malonate (1h)



¹H NMR (CDCl₃): δ = 7.62 (1H, d, *J* = 7.5 Hz), 7.33 (1H, d, *J* = 8.1 Hz), 7.22 (1H, t, *J* = 8.0 Hz), 7.11 (1H, t, *J* = 7.1 Hz), 7.07 (1H, s), 6.50 (1H, s), 4.23 (2H, t, *J* = 7.1 Hz), 3.73 (6H, s), 3.31 (1H, t, *J* = 7.1 Hz), 2.44 (2H, dt, *J* = 7.1, 7.1

Hz); ¹³C NMR (CDCl₃): δ = 169.20, 135.92, 128.70, 127.77, 121.71, 121.06, 119.55, 109.31, 101.72, 52.72, 48.74, 43.72, 29.28; HRMS (ESI): m/z calcd for C₁₅H₁₇NO₄Na [M+Na]⁺ 298.1055. Found 298.1044.

dimethyl 2-(3-(1H-indol-1-yl)propyl)malonate (1i)



¹H NMR (CDCl₃): δ = 7.63 (1H, d, *J* = 8.0 Hz), 7.32 (1H, d, *J* = 8.0 Hz), 7.20 (1H, t, *J* = 7.4 Hz), 7.09 (1H, m), 6.49 (1H, s), 4.15 (2H, t, *J* = 7.2 Hz), 3.70 (6H, s), 3.34 (1H, t, *J* = 7.2 Hz), 1.91 (4H, m); ¹³C NMR (CDCl₃): δ = 169.53, 135.92, 128.74, 127.77, 121.59, 121.11, 119.42, 109.32, 101.38, 52.68, 51.22, 45.96,

27.94, 26.26; HRMS (ESI): m/z calcd for $C_{16}H_{19}NO_4Na [M+Na]^+$ 312.1212. Found 312.1202.

dimethyl 2,3,4,9-tetrahydro-*1H*-carbazole-1,1-dicarboxylate (2a)



¹H NMR (CDCl₃): δ = 7.52 (1H, d, *J* = 7.6 Hz), 7.34 (1H, d, *J* = 8.5 Hz), 7.19 (1H, t, *J* = 5.8 Hz), 7.01 (1H, t, *J* = 7.2 Hz), 3.78 (6H, s), 2.77 (2H, t, *J* = 6.3 Hz), 2.46 (2H, m), 1.97 (2H, m); ¹³C NMR (CDCl₃): δ = 170.61, 136.29, 127.29, 126.70, 122.66, 119.39, 118.84, 113.90, 111.15, 55.36, 53.28, 31.09, 20.75,

20.59; HRMS (ESI): m/z calcd for $C_{16}H_{17}NO_4Na [M+Na]^+$ 310.1055. Found 310.1069.

dimethyl 6-bromo-2,3,4,9-tetrahydro-1H-carbazole-1,1-dicarboxylate (2b)



¹H NMR (CD₃OD): δ = 7.55 (1H, s), 7.26 (1H, d, *J* = 8.6 Hz), 7.17 (1H, d, *J* = 8.6 Hz), 3.77 (6H, s), 2.70 (2H, t, *J* = 5.8 Hz), 2.41 (2H, m), 1.93 (2H, m), 1.25 (2H, t, *J* = 7.5 Hz); ¹³C NMR (CDCl₃): δ = 170.35, 134.86, 128.69, 128.45, 125.37, 121.48, 113.51, 112.63, 112.54, 55.29, 53.38, 31.02, 30.91,

20.58, 20.44; HRMS (ESI): m/z calcd for $C_{16}H_{16}BrNO_4Na [M+Na]^+$ 388.0160. Found 388.0136.

dimethyl 8-bromo-2,3,4,9-tetrahydro-1H-carbazole-1,1-dicarboxylate (2c)



¹H NMR (CDCl₃): δ = 7.45 (1H, d, *J* = 8.0 Hz), 7.34 (1H, d, *J* = 7.5 Hz), 6.99 (1H, t, *J* = 8.0 Hz), 3.81 (1H, s), 2.74 (2H, t, *J* = 6.3 Hz), 2.46 (2H, m), 1.96 (2H, m); ¹³C NMR (CDCl₃): δ = 170.31, 135.05, 128.16, 127.94, 125.07, 120.61, 118.10, 115.17, 104.74, 55.33, 53.44, 31.07, 20.93, 20.44; HRMS (ESI): m/z calcd for C₁₆H₁₆BrNO₄Na [M+Na]⁺ 388.0160. Found 388.0143.

dimethyl 6-methoxy-2,3,4,9-tetrahydro-1H-carbazole-1,1-dicarboxylate (2d)



¹H NMR (CDCl₃): δ = 7.24 (1H, d, *J* = 8.6 Hz), 6.94 (1H, s), 6.86 (1H, d, *J* = 6.3 Hz), 3.85 (3H, s), 3.78 (6H, s), 2.71 (2H, t, *J* = 6.3 Hz), 2.45 (2H, m), 1.97 (2H, m); ¹³C NMR (CDCl₃): δ = 170.62, 154.07, 131.49, 128.08, 127.04, 113.64, 112.86, 111.96, 100.79, 56.10, 55.44, 53.30, 31.09, 31.09,

20.84, 20.60; HRMS (ESI): m/z calcd for C₁₇H₁₉BrNO₅Na [M+Na]⁺ 340.1161 Found 340.1165.

dimethyl 9-methyl-2,3,4,9-tetrahydro-1H-carbazole-1,1-dicarboxylate (2e)



¹H NMR (CDCl₃): δ = 7.51 (1H, d, *J* = 8.1 Hz), 7.31 (1H, d, *J* = 8.6 Hz), 7.24 (1H, d, *J* = 7.5 Hz), 7.10 (1H, t, *J* = 8.1 Hz), 3.78 (6H, s), 3.64 (3H, s), 2.81 (2H, t, *J* = 6.3 Hz), 2.50 (2H, m), 1.95 (2H, m); ¹³C NMR (CDCl₃): δ = 171.24, 137.89, 129.91, 126.06, 122.44, 119.10, 118.83, 112.68, 109.19, 56.23, 53.19,

33.89, 31.03, 21.04, 20.64 ; HRMS (ESI): m/z calcd for $C_{17}H_{19}NO_4Na$ [M+Na]⁺ 324.1212. Found 324.1222.

dimethyl 1,4-dihydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (2f)



¹H NMR (CDCl₃): δ = 7.47 (1H, d, *J* = 8.0 Hz), 7.36 (1H, d, *J* = 8.0 Hz), 7.18 (1H, t, *J* = 7.5 Hz), 7.10 (1H, t, *J* = 6.9 Hz), 3.77 (1H, s), 3.11 (2H, t, *J* = 5.8 Hz), 2.94 (2H, t, *J* = 6.9 Hz), 2.94 (2H, t, *J* = 6.3Hz); HRMS (ESI): m/z calcd for C₁₅H₁₅NO₄Na [M+Na]⁺ 296.0899. Found 296.0898.

dimethyl 7,8,9,10-tetrahydrocyclohepta[b]indole-6,6(5H)-dicarboxylate (2g)



¹H NMR (CDCl₃): δ = 7.52 (1H, d, *J* = 8.0 Hz), 7.30 (1H, 1H, *J* = 8.0 Hz), 7.16 (1H, t, *J* = 5.8 Hz), 7.10 (1H, t, *J* = 6.9 Hz), 3.80 (1H, s), 2.85 (2H, m), 2.54 (2H, m), 1.93-1.82 (4H, m); HRMS (ESI): m/z calcd for C₁₇H₁₉NO₄Na [M+Na]⁺ 324.1212. Found 324.1196.

dimethyl 2,3-dihydro-1H-pyrrolo[1,2-a]indole-1,1-dicarboxylate (2h)

NMR spectra of the obtained product were consistent with the reported one⁷.



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dimethyl 7,8-dihydropyrido[1,2-a]indole-9,9(6H)-dicarboxylate (2i)



NMR spectra of the obtained product were consistent with the reported one⁷.

dimethyl 2-(1H-indol-2-yl)-2-methylmalonate (4)



120.01, 111.23, 101.64, 54.44, 53.43, 21.20; HRMS (ESI): m/z calcd for $C_{14}H_{15}NO_4Na$ [M+Na]⁺ 284.0899. Found 284.0885.

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