Supplementary Material

A Microwave Assisted Intramolecular-Furan-Diels-Alder Approach to 4-Substituted Indoles

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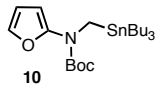
General Methods

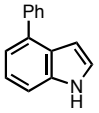
All moisture sensitive reactions were performed in flame-dried glassware under an atmosphere of nitrogen. Anhydrous tetrahydrofuran (THF) was freshly distilled from Na/benzophenone ketyl. Ethyl acetate and hexanes were freshly distilled prior to use. Unless otherwise stated, other solvents or reagents were used without further purification. Flash chromatography was performed with 40-60 μm silica gel according to the method of Still.[1] Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F-254 plates using UV light or ethanolic PMA stain for visualization. NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE 300 MHz NMR spectrometer operating at ambient temperature. Shifts are reported based on the solvent as a reference (δ 7.27 ppm for ^1H and 77.0 ppm for ^{13}C). IR samples were prepared as thin films from the deposit of a CH_2Cl_2 solution on a NaCl disk and spectra were recorded on a Nicolet AVATAR E.S.P. spectrometer. High resolution mass spectra were obtained on a Waters Autospec double focusing spectrometer (EI) or on a Waters Q-TOF mass spectrometer (ESI). Microwave reactions were performed in a Biotage Initiator laboratory microwave.



10

Furanyl Stannane 10. To a solution of 2-(*N*-Boc)-aminofuran **9**[2] (611.5 mg, 3.38 mmol) in dry DMF (4.5 mL) at 0 °C was added dry NaH (88.1 mg, 3.67 mmol) in 4 portions. The reaction mixture was stirred at 0 °C for 1 h, at which time 1-iodo-1-tributylstannylmethane (**8**)[3] (1.87 g, 4.34 mmol) was added dropwise over 5 min. The solution was stirred at 0 °C for 2 h, diluted with Et_2O (5 mL) and quenched with saturated aq. NH_4Cl (5 mL). The layers were separated and the aqueous layer was further extracted

with Et_2O (3x15 mL). The combined organic extracts were washed with water and brine and dried (Na_2SO_4). Concentration under reduced pressure and purification by chromatography on SiO_2 (5% EtOAc/hexanes) afforded **10** (1.41 g, 88%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14-7.13 (m, 1 H), 6.34-6.32 (m, 1 H), 5.93 (br s, 1 H), 3.39 (br s, 2 H), 1.50-1.40 (m, 14 H), 1.33-1.24 (m, 7 H), 0.90-0.81 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 149.9, 136.8, 110.9, 98.9, 80.5, 34.2, 28.9, 28.1, 27.3 (t, J = 27.4 Hz), 13.6, 9.7 (t, J = 157.4 Hz); HRMS (EI) calcd for $C_{18}H_{32}NO_3Sn$ ($M-C_4H_9$) 430.1404, found 430.1405.

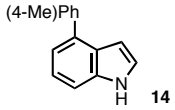


12

General Protocol for Indole Synthesis. 4-Phenylindole (12).[4] To a solution of furanyl stannane **10** (243.1 mg, 0.500 mmol) in anhydrous THF (4 mL) at -78 °C under N_2 was added a solution of *n*-BuLi (1.60 M, 0.450 mmol, 0.28 mL) dropwise over 5 min. The reaction mixture was stirred for an additional 20 min at -78 °C, then *trans*-cinnamaldehyde (2.00 mmol, 0.25 mL) was added dropwise over 2 min. The resulting solution was stirred for 3 h at -78 °C, diluted with Et_2O (3 mL) and quenched with saturated aq. NH_4Cl (4 mL). The layers were separated and the aqueous phase was further extracted with Et_2O (3x5 mL). The combined organic extracts were dried (Na_2SO_4), concentrated under reduced pressure, and purified by chromatography on SiO_2 (EtOAc/hexanes, 1:6) to afford the corresponding alcohol **11** (164.7 mg, 66%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.21 (m, 6 H), 6.70 (d, J = 15.9 Hz, 1

H), 6.36 (dd, *J* = 3.0, 2.1 Hz, 1 H), 6.20 (dd, *J* = 6.3, 15.9 Hz, 1 H), 6.06 (br s, 1 H), 4.57 (q, *J* = 5.7 Hz, 1 H), 3.78-3.75 (m, 2 H), 3.05 (br s, 1 H), 1.45 (s, 9 H).

A solution of alcohol **11** (11.0 mg, 0.03 mmol) in *o*-dichlorobenzene (2.5 mL) was heated in the microwave reactor for 20 min at 180 ^{o}C. The reaction mixture was concentrated and directly subjected to chromatography on SiO_2 (EtOAc/hexanes, 1:6) to afford **12**[4] (5.1 mg, 79%): IR (neat) 3418, 752 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (br s, 1 H), 7.76-7.72 (m, 2 H), 7.58-7.49 (m, 2 H), 7.44-7.37 (m, 2 H), 7.34-7.22 (m, 3 H), 6.78-6.76 (m, 1 H).

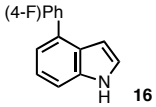


14

4-*p*-Tolyl-1*H*-indole (**14**). The intermediate furanyl alcohol **13** was prepared according to the General Protocol and isolated as a colorless oil (76%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.1 Hz, 2 H), 7.21 (dd, *J* = 0.9 Hz, 1.8 Hz, 1 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 6.66 (d, *J* = 15.9 Hz, 1 H), 6.36 (dd, *J* = 2.1, 3.3 Hz, 1 H), 6.15 (dd, *J* = 6.3, 15.9 Hz, 1 H), 6.05 (br s, 1 H), 4.51-4.50 (m, 1 H), 3.77-3.75 (m, 2 H), 3.05 (br s, 1 H), 2.35 (s, 3 H), 1.46 (s, 9 H).

Susequently, 4-(*p*-tolyl)indole **14**[5] was prepared according to the General Protocol as a colorless oil (76%): IR (neat) 3414, 752 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (br s, 1 H), 7.66-7.62 (m, 2 H), 7.42-7.38 (m, 1 H), 7.34-7.29 (m, 3 H), 7.27-7.24 (m, 1 H), 7.21 (dd, *J* = 1.2 Hz, 7.2 Hz, 1 H), 6.77-6.75 (m, 1 H), 2.46 (s, 3 H); ^{13}C NMR (75 MHz,

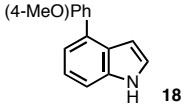
$CDCl_3$) δ 138.4, 136.6, 136.3, 134.5, 129.2, 128.6, 126.2, 124.3, 122.3, 119.6, 109.9, 102.3, 21.2.



16

4-(*p*-Fluorophenyl)-1*H*-indole (**16**). The intermediate furanyl alcohol **15** was prepared according to the General Protocol and was isolated as a colorless oil (74%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2 H), 7.19-7.18 (m, 1 H), 7.01-6.95 (m, 2 H), 6.63 (d, *J* = 15.9 Hz, 1 H), 6.34 (dd, *J* = 0.9 , 2.1 Hz, 1 H), 6.10 (dd, *J* = 6.0, 15.9 Hz, 1 H), 4.54-4.52 (m, 1 H), 3.74 (d, *J* = 6.0 Hz, 2 H), 3.18 (br s, 1 H), 1.42 (s, 9 H).

4-(*p*-Fluorophenyl)indole (**16**) was prepared according to the General Protocol and isolated as a colorless oil (83%): IR (CH_2Cl_2, film) 3410, 753 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (br s, 1 H), 7.70-7.65 (m, 2 H), 7.43-7.40 (m, 1 H), 7.31-7.26 (m, 2 H), 7.21-7.16 (m, 3 H), 6.71-6.69 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 160.5, 137.3, 136.2, 133.5, 130.2, 130.1, 126.1, 124.5, 122.3, 19.7, 115.4, 115.2, 110.3, 102.0; HRMS (EI) calcd for $C_{14}H_{10}FN$ 211.0797, found 211.0791.

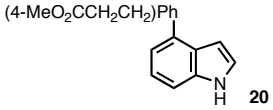


18

4-(*p*-Anisyl)indole (**18**). The intermediate furanyl alcohol **17** was prepared according to the General Protocol and isolated as a colorless oil (68%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2 H), 7.20 (dd, *J* = 0.9, 1.8 Hz, 1 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 6.61 (d, *J* = 15.6 Hz, 1 H), 6.35 (dd, *J* = 0.9, 2.1 Hz, 1 H), 6.08-6.01 (m, 2 H),

4.58-4.48 (m, 1 H), 3.80 (s, 3 H), 3.75-3.72 (m, 2 H), 3.02 (br s, 1 H), 1.44 (s, 9 H).

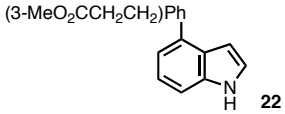
4-(*p*-Anisyl)indole (**18**) was prepared according to the General Protocol and isolated as a colorless oil (69%): IR (CH_2Cl_2) 3411, 1245, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.28 (br s, 1 H), 7.69 (d, *J* = 8.7 Hz, 2 H), 7.42-7.19 (m, 4 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 6.77 (app s, 1 H), 3.92 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 136.2, 134.1, 133.8, 129.8, 126.1, 124.2, 122.3, 119.4, 113.9, 109.7, 102.2, 55.3; HRMS (EI) calcd for $C_{15}H_{13}NO$ 223.0997, found 223.0997.



20

Methyl 3-(4-(1H-indol-4-yl)phenyl)propanoate (**20**). The intermediate furanyl alcohol **19** was prepared according to the General Protocol and isolated as a colorless oil (62%): ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.1 Hz, 2 H), 7.21-7.20 (m, 1 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 6.67 (d, *J* = 15.9 Hz, 1 H), 6.36-6.34 (m, 1 H), 6.15 (dd, *J* = 6.3, 15.9 Hz, 1 H), 6.04 (s, 1 H), 4.56-4.53 (m, 1 H), 3.75-3.73 (m, 2 H), 3.67 (s, 3 H), 2.94 (t, *J* = 7.5 Hz, 3 H), 2.62 (t, *J* = 7.8 Hz, 2 H), 1.44 (s, 9 H).

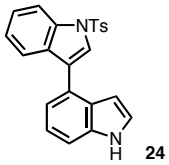
Indole **20** was prepared according to the General Protocol and isolated as a colorless oil (77%): IR (CH_2Cl_2) 3409, 1729, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.28 (br s, 1 H), 7.65 (d, *J* = 8.1 Hz, 2 H), 7.41 (d, *J* = 8.1 Hz, 1 H), 7.34-7.30 (m, 2 H), 7.28-7.25 (m, 2 H), 7.20-7.18 (m, 1 H), 6.75-6.73 (m, 1 H), 3.72 (s, 3 H), 3.05 (t, *J* = 7.8 Hz, 2 H), 2.72 (t, *J* = 7.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 139.3, 139.1, 136.2, 134.2, 128.8, 128.4, 126.1, 124.3, 122.3, 119.6, 110.1, 102.3, 51.7, 35.7, 30.7; HRMS (EI) calcd for $C_{18}H_{17}NO_2$ 279.1259, found 279.1265.



22

Methyl 3-(3-(1H-indol-4-yl)phenyl)propanoate (**22**). The intermediate furanyl alcohol **21** was prepared according to the General Protocol and isolated as a colorless oil (69%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.02 (m, 5 H), 6.69-6.62 (m, 1 H), 6.37-6.34 (m, 1 H), 6.21-6.24 (m, 1 H), 6.03 (br s, 1 H), 4.59-4.52 (m, 1 H), 3.79-3.74 (m, 2 H), 3.68 (s, 3 H), 2.97-2.89 (m, 3 H), 2.62 (t, *J* = 7.8 Hz, 2 H), 1.44 (s, 9 H).

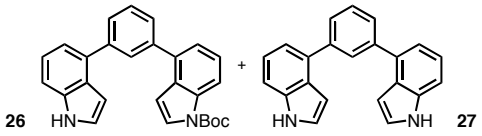
Indole **22** was prepared according to the General Protocol and was isolated as a colorless oil (81%): IR (CH_2Cl_2) 3409, 1722, 754 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (br s, 1 H), 7.60-7.58 (m, 2 H), 7.46-7.42 (m, 2 H), 7.33-7.20 (m, 4 H), 6.75 (app s, 1 H), 3.72 (s, 3 H), 3.08 (t, *J* = 7.8 Hz, 2 H), 2.74 (t, *J* = 7.8 Hz, 2 H): ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 141.5, 140.6, 136.3, 134.4, 128.7, 128.6, 126.9, 126.8, 126.2, 124.4, 122.3, 119.7, 110.2, 102.3, 51.6, 35.8, 31.1; HRMS (EI) calcd for $C_{18}H_{17}NO_2$ 279.1259, found 279.1262.



24

4-(*N*-tosyl-3-indolyl)indole (**24**). The intermediate furanyl alcohol **23** was prepared according to the General Protocol and was isolated as a waxy solid (78%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1 H), 7.77-7.69 (m, 3 H), 7.57 (s, 1 H), 7.36-7.18 (m, 5 H), 6.77 (d, *J* = 15.9 Hz, 1 H), 6.36-6.24 (m, 2 H), 6.06 (br s, 1 H), 4.63-4.55 (m, 1 H), 3.80 (d, *J* = 6.0 Hz, 2 H), 3.21 (br s, 1 H), 2.32 (s, 3 H), 1.43 (s, 9 H).

4-(*N*-tosyl-3-indolyl)indole (**24**) was prepared according to the General Protocol and was isolated as a colorless oil (71%): IR (CH_2Cl_2) 3422, 748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (br s, 1 H), 8.13 (d, *J* = 8.4 Hz, 1 H), 7.88-7.85 (m, 3 H), 7.76 (d, *J* = 7.8 Hz, 1 H), 7.48-7.25 (m, 8 H), 6.64 (app s, 1 H), 2.37 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 136.2, 135.4, 130.1, 129.9, 126.9, 126.6, 125.2, 124.8, 124.4, 123.9, 123.3, 123.1, 122.1, 121.2, 120.2, 113.7, 110.6, 102.4, 21.6; HRMS (EI) calcd for $C_{23}H_{18}N_2O_2S$ 386.1089, found 386.1083.

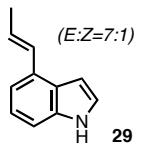


Tert-butyl 4-(3-(1H-indol-4-yl)phenyl)-1*H*-indole-1-carboxylate (**26**). To a solution of the furanyl stannane **10** (486.2 mg, 1.000 mmol) in anhydrous THF (4 mL) at -78 ^oC under N_2 was added a solution of *n*-BuLi (1.60 M, 0.900 mmol, 0.56 mL) dropwise over 5 min. The reaction mixture was stirred for an additional 20 min at -78 ^oC, then a solution of (*E*,*E*)-3,3'-(1,3-phenylene)bis-2-propenal (47.0 mg, 0.250 mmol) in THF (1 mL) was added dropwise over 2 min. The resulting solution was stirred for 3 h at -78 ^oC, diluted with Et_2O (3 mL) and quenched with saturated aq. NH_4Cl (4 mL). The layers were separated and the aqueous phase was further extracted with Et_2O (3x5 mL). The combined organic extracts were dried (Na_2SO_4), concentrated under reduced pressure, and purified by chromatography on SiO_2 (EtOAc/hexanes, 1:4) to afford alcohol **25** as an amorphous solid (130.4 mg, 89%): ^1H NMR (300 MHz, $CDCl_3$) δ 7.32-7.19 (m, 6 H), 6.65 (d, *J* = 15.9 Hz, 2 H), 6.36-6.34 (m, 2 H), 6.18 (dd, *J* = 6.0, 15.9 Hz, 2

H), 6.03 (br s, 2 H), 4.60-4.50 (m, 2 H), 3.76-3.74 (m, 4 H), 3.12 (br s, 2 H), 1.43 (s, 18 H).

A Diels-Alder reaction according to the General Protocol afforded a 7:4 mixture of **26** and **27** (61%) as colorless oils. **26**: R_F 0.35 (EtOAc/hexanes, 1:3); IR (CH_2Cl_2) 3415, 1732, 1138, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.32 (br s, 1 H), 8.23 (d, *J* = 6.9 Hz, 1 H), 7.99 (s, 1 H), 7.79-7.77 (m, 1 H), 7.68-7.62 (m, 3 H), 7.47-7.40 (m, 3 H), 7.37-7.29 (m, 3 H), 6.86-6.83 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 141.6, 140.6, 136.3, 135.6, 134.9, 134.3, 129.2, 128.8, 128.7, 127.7, 127.5, 126.1, 124.5, 122.8, 122.3, 119.9, 114.2, 110.3, 106.7, 102.2, 83.7, 28.2; HRMS (ESI) calcd for $C_{27}H_{25}N_2O_2$ (M+H) 409.1916, found 409.1927.

27: R_F 0.15 (EtOAc/hexanes, 1:3); IR (CH_2Cl_2) 3410, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 (br s, 2 H), 8.04 (app t, *J* = 1.5 Hz, 1 H), 7.73-7.70 (m, 2 H), 7.60-7.55 (m, 1 H), 7.42-7.37 (m, 2 H), 7.34-7.23 (m, 6 H), 6.81-6.79 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 136.3, 134.6, 129.1, 128.6, 127.4, 126.2, 124.4, 122.3, 119.9, 110.2, 102.4; HRMS (EI) calcd for $C_{22}H_{17}N_2$ (M+H) 308.1313, found 308.1316.

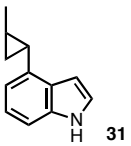


29

4-(1-Propenyl)indole (**29**). The intermediate furanyl alcohol **28** was prepared according to the General Protocol and was isolated as a colorless oil (81%): ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 0.9, 2.1 Hz, 1 H), 6.33 (dd, *J* = 1.8, 3.0 Hz, 1 H), 6.25 (dd, *J* = 10.5, 15.3 Hz, 1 H), 6.06-5.97 (m, 2 H), 5.76-5.63 (m, 1 H), 5.51 (dd, *J* = 6.6,

15.3 Hz, 1 H), 4.40-4.31 (m, 1 H), 3.69-3.61 (m, 1 H), 2.83 (br s, 1 H), 1.74 (d, *J* = 6.6 Hz, 3 H), 1.43 (s, 9 H).

4-(1-Propenyl)indole (**29**) was prepared according to the General Protocol and was isolated as a 7:1 ratio of inseparable oily olefin isomers (69%). Major isomer: IR (CH_2Cl_2) 3410, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (br s, 1 H), 7.31-7.16 (m, 4 H), 6.88-6.78 (m, 2 H), 6.45 (ddq, *J* = 15.9, 1.8, 6.6 Hz, 1 H), 2.01 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 130.4, 129.3, 126.5, 125.7, 124.0, 122.1, 116.7, 109.5, 101.2, 18.9; HRMS (EI) calcd for $C_{11}H_{11}N$ 157.0891, found157.0889.

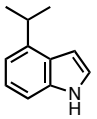


31

4-(2-Methylcyclopropyl)-1*H*-indole (**31**). To a solution of the furanyl stannane (**10**) (0.30 g, 0.617 mmol) in anhydrous THF (9 mL) at -78 °C under N_2 was added a solution of *n*-BuLi (1.60 M, 0.617 mmol, 0.38 mL) in hexanes dropwise over 5 min. The reaction mixture was stirred for an additional 1 h at -78 °C. A solution of (*E*)-3-(2-methylcyclopropyl)acrylaldehyde (0.586 mmol, 64.6 mg) in THF (2 mL) was added dropwise over 5 min. The resulting solution was stirred for 3 h at -78 °C, then quenched with saturated aq. NH_4Cl (5 mL). The layers were separated and the aqueous phase was further extracted with Et_2O (3x10 mL). The combined organic extracts were dried (Na_2SO_4), concentrated under reduced pressure, and purified by chromatography on SiO_2 (EtOAc/hexanes, 95:5 to 9:1) to afford alcohol **30** (124.2 mg, 65%) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (s, 1 H), 6.34 (s, 1 H), 6.02 (s, 1 H), 5.45 (dd, *J* = 15.3, 6.6 Hz, 1 H), 5.28 (dd, *J* = 15.3, 8.7 Hz, 1 H), 4.31-4.22 (m, 1 H), 3.64-3.62 (m, 2 H),

1.48 (s, 9 H), 1.05 (d, *J* = 5.7 Hz, 3 H), 0.80-0.70 (m, 1 H), 0.57-0.51 (m, 1 H), 0.50-0.46 (m, 1 H).

According to the General Protocol, alcohol **30** (20.1 mg) was converted to the colorless oily indole **31** (5.4 mg, 48%): ATR-IR (neat) 3401, 2948, 1580, 1500, 1338, 1075, 745 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (br s, 1 H), 7.23-7.21 (m, 2 H), 7.11 (app t, *J* = 7.5 Hz, 1 H), 6.73-6.67 (m, 2 H), 1.99-1.93 (m, 1 H), 1.28 (d, *J* = 5.4 Hz, 3 H), 1.28-1.16 (m, 1 H), 1.10-1.05 (m, 1 H), 0.82-0.76 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 135.5, 123.4, 122.2, 114.8, 108.2, 101.1, 22.1, 19.4, 16.6, 16.1; HRMS (EI) calcd for $C_{12}H_{13}N$ 171.1048, found: 171.1047.

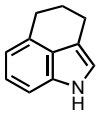


33

4-*Iso*-propyl-1*H*-indole (**33**). To a solution of the furanyl stannane **10** (0.33 g, 0.689 mmol) in anhydrous THF (10 mL) at -78 °C under N_2 was added a solution of *n*-BuLi (1.60 M, 0.689 mmol, 0.43 mL) in hexanes dropwise over 5 min. The reaction mixture was stirred for an additional 1 h at -78 °C. A solution of (*E*)-4-methylpent-2-enal (0.65 mmol, 64.0 mg) in THF (2 mL) was added dropwise over 5 min. The resulting solution was stirred for 3 h at -78 °C, then quenched with saturated aq. NH_4Cl (5 mL). The layers were separated and the aqueous phase was further extracted with Et_2O (3x20 mL). The combined organic extracts were dried (Na_2SO_4), concentrated under reduced pressure, and purified by chromatography on SiO_2 (EtOAc/hexanes, 9:1) to afford the alcohol **32** (72.3 mg, 36%) as a yellowish oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.19-7.18 (m, 1 H), 6.34 (dd, *J* = 3.0, 2.4 Hz, 1 H), 6.02 (bs, 1 H), 5.72 (dd, *J* = 15.3, 6.6 Hz, 1 H),

5.39 (ddd, *J* = 15.3, 8.7, 0.9 Hz, 1 H), 4.33-4.26 (m, 1 H), 3.71-3.57 (m, 2 H), 2.6 (bs, 1 H), 2.33-2.21 (m, 1 H), 1.44 (s, 9 H), 0.97 (d, *J* = 5.7 Hz, 3 H).

According to the General Protocol, alcohol **32** (26.3 mg) was converted to the colorless oily indole **33** (5.1 mg, 36%): ATR-IR (neat) 3401, 2956, 2866, 1498, 1409, 1340, 743 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 8.26 (br s, 1 H), 7.25 (d, *J* = 8.1 Hz, 1 H), 7.22 (t, *J* = 2.7 Hz, 1 H), 7.17-7.11 (m, 1 H), 6.98 (d, *J* = 7.2 Hz, 1 H), 6.65-6.62 (m, 1 H), 3.38 (sept, *J* = 7.2 Hz, 1 H), 1.38 (d, *J* = 6.9 Hz, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 141.6, 136.4, 127.1, 124.0, 122.7, 115.9, 109.3, 101.4, 31.9, 23.5; HRMS (EI) calcd for $C_{11}H_{13}N$ 159.1048, found 159.1047.



35

2,6,7,8-Tetrahydrobenzo[*c,d*]indole (**35**). To a solution of the furanyl stannane **10** (250.0 mg, 0.5141 mmol) in anhydrous THF (7.5 mL) at -78 °C under N_2 was added a solution of *n*-BuLi (1.60 M, 0.514 mmol, 0.32 mL) in hexanes dropwise over 10 min. The resulting mixture was stirred for an additional 1 h at -78 °C. A solution of 2-cyclohexene-1-one (2.5706 mmol, 247.1 mg) in THF (1.5 mL) was added dropwise over 5 min. The resulting solution was stirred for 1 h at -78 °C, then quenched with saturated aq. NH_4Cl (5 mL) and extracted with Et_2O (3x20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), concentrated under reduced pressure, and purified by chromatography on SiO_2 (EtOAc/hexanes, 9:1) to afford the alcohol **34** (75.6 mg, 51%) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (br s, 1 H), 6.36-6.33 (m,

1 H), 6.00 (bs, 1 H), 5.82 (app dt, *J* = 9.9, 3.0 Hz, 1 H), 5.58 (d, *J* = 9.9 Hz, 1 H), 3.75, (d of AB, *J* = 0.9, 14.7 Hz, 1 H), 3.69 (d of AB, *J* = 1.2, 14.7 Hz, 1 H), 2.10-1.56 (m, 6 H), 1.44 (s, 9 H).

A Diels-Alder reaction according to the General Protocol afforded indole **35** (84%) as a white solid: Mp 48.6-50.2 °C; ATR-IR (neat) 3399, 2920, 2833, 1439, 1081, 1025, 745. cm^{-1}; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.92 (br s, 1 H), 7.12 (d, *J* = 4.2 Hz, 1 H), 7.06 (t, *J* = 3.3 Hz, 1 H), 6.86 (s, 1 H), 6.78 (d, *J* = 3.3 Hz, 1 H), 2.92 (t, *J* = 3.0 Hz, 2 H), 2.85 (dt, *J* = 3.3, 0.3 Hz, 2 H), 2.04 (app quint, *J* = 3.0 Hz, 2 H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 134.5, 132.8, 127.7, 123.0, 117.7, 116.1, 114.3, 108.5, 28.0, 25.3, 22.4; HRMS (EI) calcd for $C_{11}H_{11}N$ 157.0891, found 157.0894.

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