Platinum-Catalyzed Intramolecular Alkylation of Indoles with Unactivated Olefins

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Supporting Information

Experimental procedures, analytical and spectroscopic data for indoles, copies of 2-D NMR spectra for *anti*-**5**-*d*₂, and X-ray crystal structure data for **5** (38 pages).

Experimental

General Methods. Catalytic reactions were performed in a thick-walled pressure tube (Ace Glass) under a nitrogen atmosphere. NMR spectra were obtained on a Varian spectrometer operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR in CDCl_3 unless otherwise noted. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. Gas chromatography was performed on a Hewlett-Parkard 5890 gas chromatography equipped with a 25 m polydimethylsiloxane capillary column. Flash column chromatography was performed employing 200-400 mesh silica gel (EM). Thin layer chromatography (TLC) was performed on silica gel 60 F₂₅₄. Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). 1,4-Dioxane (Acros, anhydrous) and HCl solution (4.0 M, 1,4-dioxane, Aldrich) were stored in an inert atmosphere glovebox. $[\text{PtCl}_2(\text{H}_2\text{C}=\text{CH}_2)]_2$, $\text{PtCl}_2(\text{MeCN})_2$ and PtCl_2 (Strem), methyl 4-pentenoate, ethyl 5-methyl-5-hexenoate, *cis*-2-penten-1-ol, *trans*-2-penten-1-ol, 1-methyl-1*H*-indole-2-carboxylic acid (Aldrich), and 3-chloro-1-cyclohexene (TCI) were used as received. . *N*-Trimethylsilyl-*o*-toluidine (**S1**),¹ 2-(3-butenyl)-1*H*-indole,² methyl 2,2-dimethyl-5-hexenoate,³ methyl 2,2-dimethyl-4-pentenoate,⁴ 2-hydroxymethyl-1-methyl-1*H*-indole (**S2**),⁵ *N*-allyl-*N*-methyl 1*H*-indole-2-carboxamide,⁶ and 1,3-dideuterio-2-cyclohexen-1-ol⁷ were synthesized employing published procedures. (*R*)-6,2'-bis-[bis-(3,5-di-*tert*-butyl-4-methoxyphenyl)-phosphino]-2,6'-dimethoxybiphenyl [(*R*)-**S3**] and (*R*)-3,5-*i*-Pr-MeOBIPHEP were provided by Dr. Rudolph Schmid (Hoffmann-LaRoche).

2-Alkenyl Indoles

1-Methyl-2-(4-pentenyl)-1*H*-indole (1). *n*-BuLi (2.5 M solution in hexanes, 26.0 mL, 65.0 mmol) was added dropwise to a solution of **S1** (4.70 g, 26.0 mmol) in hexanes (150

mL) at 0 °C. The resulting orange solution was refluxed for 6 h, cooled to -78 °C, and treated with a solution of methyl 5-hexenoate (6.25 g, 44.0 mmol) in THF (25 mL). The resulting mixture was warmed to room temperature, stirred for 1 h, and quenched with brine. The aqueous layer was extracted with ether (2 × 100 mL) and the layers were separated. The combined organic extracts were dried (MgSO₄) and concentrated under vacuum. Column chromatography of the residue (SiO₂; hexanes–CH₂Cl₂ = 5:1) gave 2-(4-pentenyl)-1*H*-indole (**S4**) (2.99 g, 62%) as a yellow oil. Compound **S4** (196 mg, 1.1 mmol) and MeI (137 µL, 2.2 mmol) were added sequentially to a suspension of KOH (560 mg, 10.0 mmol) in acetone (5 mL). The resulting mixture was stirred at room temperature for 3 h and quenched with water. The layers were separated and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic extracts were washed (brine), dried (MgSO₄), and concentrated under vacuum. Column chromatography of the residue (SiO₂; hexanes–CH₂Cl₂ = 30:1) gave **1** (162 mg, 77%) as a pale yellow oil.

For S4: TLC (hexanes–CH₂Cl₂ = 1:1): *R_f* = 0.59. ¹H NMR: δ 7.80 (s, 1 H), 7.59-7.57 (m, 1 H), 7.32-7.29 (m, 1 H), 7.16 (dt, *J* = 1.6, 7.6 Hz, 1 H), 7.12 (dt, *J* = 1.2, 7.4 Hz, 1 H), 6.29-6.28 (m, 1 H), 5.88 (tdd, *J* = 6.8, 10.4, 17.2 Hz, 1 H), 5.13-5.04 (m, 2 H), 2.78 (t, *J* = 7.6 Hz, 2 H), 2.19 (q, *J* = 7.2 Hz, 2 H), 1.85 (quint, *J* = 7.2 Hz, 2 H). ¹³C{¹H} NMR: δ 139.8, 138.5, 136.1, 129.1, 121.3, 120.1, 119.9, 115.5, 110.6, 99.9, 33.5, 28.6, 27.9. IR (neat, cm⁻¹): 3404, 2931, 1456, 1415, 1287, 911, 781, 749. Anal. calcd (found) for C₁₃H₁₅N: C, 84.28 (84.21); H, 8.16 (8.11).

For 1: TLC (hexanes–CH₂Cl₂ = 5:1): *R_f* = 0.68. ¹H NMR: δ 7.58 (br d, *J* = 7.6 Hz, 1 H), 7.30 (dd, *J* = 0.8, 8.0 Hz, 1 H), 7.20 (ddd, *J* = 1.2, 7.6, 8.0 Hz, 1 H), 7.11 (dt, *J* = 1.2, 7.8 Hz, 1 H), 6.30 (d, *J* = 0.8 Hz, 1 H), 5.91 (tdd, *J* = 6.8, 10.4, 17.2 Hz, 1 H), 5.15-5.05 (m, 2 H), 3.69 (s, 3 H), 2.79 (t, *J* = 7.6 Hz, 2 H), 2.25 (tq, *J* = 1.2, 6.8 Hz, 2 H), 1.87 (quint, *J*

= 7.6 Hz, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 141.3, 138.5, 137.7, 128.2, 120.8, 120.1, 119.5, 115.5, 109.0, 99.1, 33.7, 29.7, 28.1, 26.5. IR (neat, cm^{-1}): 3060, 2933, 1456, 1312, 911, 772, 747. Anal. calcd (found) for $\text{C}_{14}\text{H}_{17}\text{N}$: C, 84.37 (84.14); H, 8.60 (8.76).

1-Benzyl-2-(4-pentenyl)-1*H*-indole (Table 1, entry 2). A solution of **S4** (0.66 g, 3.5 mmol) in DMF (5 mL) was added to a suspension of NaH (85 mg, 3.5 mmol) in DMF (5 mL) at 0 °C. The resulting mixture was stirred for 10 min and treated with a solution of benzylchloride (0.45 g, 3.5 mmol) in DMF (3 mL). The resulting suspension was warmed to room temperature, stirred for 4 h, and quenched with aqueous 1 N HCl. The layers were separated and the aqueous layer was extracted with ether (3×10 mL). The combined organic extracts were washed (brine), dried (MgSO_4), and concentrated under vacuum. Column chromatography of the residue (SiO_2 ; hexanes–ether = 25:1) gave 1-benzyl-2-(4-pentenyl)-1*H*-indole (0.89 g, 73%) as a yellow oil. TLC (hexanes–EtOAc = 5:1): R_f = 0.72. ^1H NMR: δ 7.66–7.63 (m, 1 H), 7.32–7.20 (m, 5 H), 7.17–7.12 (m, 2 H), 7.00–6.98 (m, 2 H), 6.41 (d, J = 0.8 Hz, 1 H), 5.84 (tdd, J = 6.8, 10.4, 17.2 Hz, 1 H), 5.34 (s, 2 H), 5.09–5.00 (m, 2 H), 2.73 (t, J = 7.6 Hz, 2 H), 2.19 (tq, J = 1.2, 6.8 Hz, 2 H), 1.84 (quint, J = 7.6 Hz, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 141.2, 138.3, 137.4, 128.9, 128.5, 128.3, 127.4, 126.1, 121.0, 120.0, 119.7, 115.3, 109.5, 99.7, 46.6, 33.5, 27.7, 26.2. IR (neat, cm^{-1}): 3050, 3027, 2926, 2860, 1494, 1465, 1452, 1314, 735, 696. HRMS calcd (found) for $\text{C}_{20}\text{H}_{21}\text{N}$ (M^+): 275.1674 (275.1684).

5-Methoxy-1-methyl-2-(4-pentenyl)-1*H*-indole (Table 1, entry 3). 5-Methoxy-2-(4-pentenyl)-1*H*-indole (**S5**) was isolated in 30% yield as a yellow oil from reaction of **S1** and methyl 5-hexenoate employing a procedure similar to that used to synthesize **S4**. 5-Methoxy-1-methyl-2-(4-pentenyl)-1*H*-indole was isolated in 53% yield as a pale yellow oil from **S5** and methyl iodide employing a procedure similar to that used to synthesize **1**.

For S5: TLC (hexanes– CH_2Cl_2 = 1:2): R_f = 0.44. ^1H NMR: δ 7.79 (s, 1 H), 7.18 (dd, J

= 0.8, 8.8 Hz, 1 H), 7.04 (d, $J = 2.4$ Hz, 1 H), 6.80 (ddd, $J = 0.8, 2.8, 8.8$ Hz, 1 H), 6.20-6.19 (m, 1 H), 5.85 (tdd, $J = 6.8, 10.4, 17.2$ Hz, 1 H), 5.10-5.00 (m, 2 H), 3.86 (s, 3 H), 2.74 (t, $J = 7.6$ Hz, 2 H), 2.16 (q, $J = 7.2$ Hz, 2 H), 1.82 (quint, $J = 7.2$ Hz, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 154.4, 140.7, 138.5, 131.3, 129.6, 115.4, 111.3, 111.1, 102.3, 99.8, 56.2, 33.5, 28.6, 27.9. IR (neat, cm^{-1}): 3405, 2936, 1456, 1588, 1485, 1453, 1168, 1032, 913. HRMS calcd (found) for $\text{C}_{14}\text{H}_{17}\text{O}_2$ (M^+): 215.1310 (215.1310).

For 5-Methoxy-1-methyl-2-(4-pentenyl)-1H-indole: TLC (hexanes- $\text{CH}_2\text{Cl}_2 = 1:2$): $R_f = 0.59$. ^1H NMR: δ 7.18 (br d, $J = 8.8$ Hz, 1 H), 7.06 (br d, $J = 2.4$ Hz, 1 H), 6.84 (dd, $J = 2.4, 8.8$ Hz, 1 H), 6.22 (s, 1 H), 5.89 (tdd, $J = 6.4, 10.4, 17.2$ Hz, 1 H), 5.14-5.04 (m, 2 H), 3.87 (s, 3 H), 3.65 (s, 3 H), 2.75 (t, $J = 7.8$ Hz, 2 H), 2.23 (q, $J = 7.2$ Hz, 2 H), 1.85 (quint, $J = 7.6$ Hz, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 154.3, 141.9, 138.5, 133.0, 128.5, 115.5, 110.7, 109.7, 102.3, 98.8, 56.3, 33.6, 29.8, 28.1, 26.5. IR (neat, cm^{-1}): 2936, 1620, 1486, 1403, 1214, 1147, 1033, 911. Anal. calcd (found) for $\text{C}_{15}\text{H}_{19}\text{NO}$: C, 78.56 (78.74); H, 8.35 (8.37).

cis-2-(2,2-Dicarbomethoxy-4-heptenyl)-1-methyl-1H-indole (Table 1, entry 4). *n*-BuLi (2.5 M solution in hexanes, 10.5 mL, 26.3 mmol) was added to a solution of **S2** (4.03 g, 25.0 mmol) in THF (50 mL) at -78°C . After 2 min, MsCl (3.11 g, 27.5 mmol) and LiBr (6.53 g, 75.0 mmol) were added sequentially. The resulting mixture was warmed at 0°C , stirred for 30 min, and transferred via cannula to a solution of sodium dimethyl malonate in THF [generated from dimethyl malonate (6.60 g, 50.0 mmol) and NaH (1.20 g, 50.0 mmol) in THF (100 mL)]. The resulting mixture was stirred at room temperature for 2 h and quenched with water. The layers were separated and the aqueous layer was extracted with ether (3×150 mL). The combined organic extracts were washed (brine), dried (MgSO_4) and concentrated under vacuum. Column chromatography of the residue (SiO_2 ; hexanes-EtOAc = 5:1) gave dimethyl 2-(1-methyl-1H-indol-2-ylmethyl)malonate (**S6**) (2.54 g, 37%) as a pale yellow solid. *n*-BuLi (2.5 M solution

in hexanes, 5.1 mL, 12.6 mmol) was added to a solution of *cis*-2-penten-1-ol (1.03 g, 12.0 mmol) in THF (10 mL) at -78°C . After stirring for 2 min, MsCl (1.49 g, 13.2 mmol) and LiBr (3.13 g, 36.0 mmol) were added sequentially. The resulting mixture was warmed to 0°C , stirred for 30 min, and transferred via cannula to a solution of sodium dimethyl 2-(1-methyl-1*H*-indol-2-ylmethyl)malonate [prepared from **S6** (1.10 g, 4.0 mmol) and NaH (97 mg, 4.05 mmol) in THF (10 mL)]. The resulting mixture was stirred at room temperature for 3 h and quenched with water. The layers were separated and the aqueous layer was extracted with ether (3×30 mL). The combined organic extracts were washed (brine), dried (MgSO_4), and concentrated under vacuum. Column chromatography of the residue (SiO_2 ; hexanes–EtOAc = 5:1) gave *cis*-2-(2,2-dicarbomethoxy-4-heptenyl)-1-methyl-1*H*-indole (0.75 g, 55%) as a viscous yellow oil.

For S6: mp $87\text{--}89^{\circ}\text{C}$. TLC (hexanes–EtOAc = 2:1): $R_f = 0.45$. ^1H NMR: δ 7.53 (br d, $J = 8.0$ Hz, 1 H), 7.28 (br d, $J = 8.4$, 1 H), 7.18 (br t, $J = 7.2$ Hz, 1 H), 7.10–7.06 (m, 1 H), 6.27 (s, 1 H), 3.88 (t, $J = 7.6$ Hz, 1 H), 3.76 (s, 6 H), 3.71 (s, 3 H), 3.41 (d, $J = 7.6$ Hz, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 169.3, 137.8, 136.9, 128.0, 121.5, 120.4, 119.8, 109.3, 99.9, 53.2, 51.4, 29.8, 26.3. IR (neat, cm^{-1}): 2949, 1757, 1732, 1649, 1434, 749. Anal. calcd (found) for $\text{C}_{15}\text{H}_{17}\text{NO}_4$: C, 65.44 (65.22); H, 6.22 (6.17).

For *cis*-2-(2,2-Dicarbomethoxy-4-heptenyl)-1-methyl-1*H*-indole: TLC (hexanes–EtOAc = 2:1): $R_f = 0.64$. ^1H NMR: δ 7.53 (br d, $J = 7.6$ Hz, 1 H), 7.27 (br d, $J = 8.0$ Hz, 1 H), 7.18 (dt, $J = 1.2, 7.6$ Hz, 1 H), 7.10–7.06 (m, 1 H), 6.26 (s, 1 H), 5.60–5.53 (m, 1 H), 5.31–5.23 (m, 1 H), 3.74 (s, 6 H), 3.67 (s, 3 H), 3.45 (s, 2 H), 2.82 (dd, $J = 1.0, 7.4$ Hz, 2 H), 1.94 (d quint, $J = 1.2, 7.4$ Hz, 2 H), 0.89 (t, $J = 7.6$ Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 171.7, 137.5, 136.5, 135.1, 128.1, 122.1, 121.4, 120.4, 119.8, 109.3, 101.2, 58.0, 53.0, 30.3, 30.0, 29.3, 20.9, 14.3. IR (neat, cm^{-1}): 2954, 1737, 1468, 1434, 1318, 1289, 1214, 750. Anal. calcd (found) for $\text{C}_{20}\text{H}_{25}\text{NO}_4$: C, 69.95 (69.94); H, 8.16 (8.29).

***trans*-2-(2,2-Dicarbomethoxy-4-heptenyl)-1-methyl-1*H*-indole** (Table 1, entry 5). *trans*-2-(2,2-Dicarbomethoxy-4-heptenyl)-1-methyl-1*H*-indole was isolated in 81% yield as a viscous yellow oil from reaction of *trans*-2-penten-1-ol and **S6** employing a procedure similar to that used to synthesize *cis*-2-(2,2-dicarbomethoxy-4-heptenyl)-1-methyl-1*H*-indole. TLC (hexanes–EtOAc = 2:1): R_f = 0.68. ^1H NMR: δ 7.55-7.53 (m, 1 H), 7.28 (dd, J = 0.8, 8.0 Hz, 1 H), 7.19 (dt, J = 1.2, 7.6 Hz, 1 H), 7.09 (dt, J = 1.2, 8.0 Hz, 1 H), 6.27 (d, J = 0.8 Hz, 1 H), 5.58-5.51 (m, 1 H), 5.37-5.29 (m, 1 H), 3.74 (s, 6 H), 3.68 (s, 3 H), 3.43 (s, 2 H), 2.76 (dd, J = 1.0, 7.4 Hz, 2 H), 2.06-1.99 (m, 2 H), 0.97 (t, J = 7.4 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 171.6, 137.8, 137.5, 135.2, 128.1, 122.7, 121.4, 120.4, 119.8, 109.4, 101.2, 58.5, 52.9, 36.0, 30.0, 29.3, 26.0, 14.1. IR (neat, cm^{-1}): 2955, 1737, 1468, 1434, 1210, 971, 749. Anal. calcd (found) for $\text{C}_{20}\text{H}_{25}\text{NO}_4$: C, 69.95 (69.80); H, 7.34 (7.28).

1-Methyl-2-(4-methyl-4-pentenyl)-1*H*-indole (Table 1, entry 6). 2-(4-Methyl-4-pentenyl)-1*H*-indole (**S7**) was isolated in 45% yield as a yellow oil from reaction of **S1** and ethyl 5-methyl-5-hexenoate employing a procedure similar to that used to synthesize **S4**. 1-Methyl-2-(4-methyl-4-pentenyl)-1*H*-indole was isolated in 80% yield as a yellow oil from reaction of **S7** and methyl iodide employing a procedure similar to that used to synthesize **1**.

For S7: TLC (hexanes– CH_2Cl_2 = 1:1): R_f = 0.57. ^1H NMR: δ 7.82 (s, 1 H), 7.58-7.56 (m, 1 H), 7.32-7.30 (m, 1 H), 7.18-7.09 (m, 2 H), 6.28 (dd, J = 0.8, 2.0 Hz, 1 H), 4.81-4.80 (m, 1 H), 4.76-4.75 (m, 1 H), 2.76 (t, J = 7.4 Hz, 2 H), 2.15 (t, J = 7.4 Hz, 2 H), 1.89 (quint, J = 7.4 Hz, 2 H), 1.78 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 145.6, 139.9, 136.1, 129.1, 121.3, 120.1, 119.9, 110.7, 110.6, 99.9, 37.5, 28.0, 27.3, 22.7. IR (neat, cm^{-1}): 3405, 2937, 1455, 1394, 749. Anal. calcd (found) for $\text{C}_{14}\text{H}_{17}\text{N}$: C, 84.37 (84.22); H, 8.60 (8.70).

For 1-Methyl-2-(4-methyl-4-pentenyl)-1*H*-indole: TLC (hexanes– CH_2Cl_2 = 5:1): R_f = 0.35. ^1H NMR: δ 7.63-7.61 (m, 1 H), 7.33 (br d, J = 7.6 Hz, 1 H), 7.23 (dt, J = 1.2, 6.8

Hz, 2 H), 7.15 (dt, $J = 1.0, 7.6$ Hz, 1 H), 6.34 (d, $J = 0.4$ Hz, 1 H), 4.86-4.82 (m, 2 H), 3.71 (s, 3 H), 2.79 (t, $J = 7.4$ Hz, 2 H), 2.24 (t, $J = 7.4$ Hz, 2 H), 1.95 (quint, $J = 7.4$ Hz, 2 H), 1.83 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 145.6, 141.4, 137.6, 128.2, 120.8, 120.0, 119.5, 110.7, 109.0, 99.1, 37.7, 29.7, 26.7, 26.6, 22.7. IR (neat, cm^{-1}): 2933, 1643, 1470, 742. Anal. calcd (found) for $\text{C}_{15}\text{H}_{19}\text{N}$: C, 84.46 (84.61); H, 8.98 (8.83).

2-(1,1-Dimethyl-4-pentenyl)-1-methyl-1*H*-indole (Table 1, entry 7). 2-(1,1-Dimethyl-4-pentenyl)-1-methyl-1*H*-indole was isolated in 34% yield as a pale yellow oil from reaction of 2-(1,1-dimethyl-4-pentenyl)-1*H*-indole and methyl iodide employing a procedure similar to that used to synthesize **1**. TLC (hexanes- $\text{CH}_2\text{Cl}_2 = 5:1$): $R_f = 0.36$. ^1H NMR: δ 7.59-7.57 (m, 1 H), 7.31 (dd, $J = 0.8, 8.0$ Hz, 1 H), 7.21 (ddd, $J = 1.2, 7.6, 8.0$ Hz, 1 H), 7.11 (ddd, $J = 1.2, 6.8, 7.6$ Hz, 1 H), 6.35 (d, $J = 0.4$ Hz, 1 H), 5.85-5.75 (m, 1 H), 5.00-4.91 (m, 2 H), 3.88 (s, 3 H), 1.92-1.90 (m, 4 H), 1.51 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 147.4, 139.1, 138.7, 127.5, 121.5, 120.2, 119.6, 114.5, 108.9, 100.3, 41.0, 36.1, 29.7, 32.6, 29.7, 29.2. IR (neat, cm^{-1}): 2978, 1469, 1356, 1313, 781, 749. Anal. calcd (found) for $\text{C}_{16}\text{H}_{21}\text{N}$: C, 84.53 (84.42); H, 9.31 (9.29).

2-(1,1-Dimethyl-4-pentenyl)-1*H*-indole (Table 1, entry 8). 2-(1,1-Dimethyl-4-pentenyl)-1*H*-indole was isolated in 45% yield as a pale yellow solid from reaction of **S1** and methyl 2,2-dimethyl-5-hexenoate employing a procedure similar to that used to synthesize **S4**. mp 42-44 °C. TLC (hexanes- $\text{CH}_2\text{Cl}_2 = 1:1$): $R_f = 0.60$. ^1H NMR: δ 7.93 (s, 1 H), 7.60-7.58 (m, 1 H), 7.36-7.34 (m, 1 H), 7.19-7.10 (m, 2 H), 6.30 (dd, $J = 1.0, 2.2$, 1 H), 5.80 (tdd, $J = 6.4, 10.2, 17.0$ Hz, 1 H), 5.03-4.92 (m, 2 H), 1.99-1.93 (m, 2 H), 1.77-1.74 (AA'XX', 2 H), 1.42 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 147.2, 139.2, 136.2, 128.8, 121.4, 120.3, 119.9, 114.5, 110.7, 98.8, 43.0, 35.3, 29.5, 28.3. IR (neat, cm^{-1}): 3424, 2966, 1455, 1290, 909, 786, 750. Anal. calcd (found) for $\text{C}_{15}\text{H}_{19}\text{N}$: C, 84.46 (84.26); H, 8.98 (9.12).

Dimethyl 2-(2-cyclohexenyl)-2-(1-methyl-1*H*-indol-2-ylmethyl)malonate (4,

Table 1, entry 9). A solution of **S6** (470 mg, 1.71 mmol) in THF (5 mL) was added to a suspension of NaH (43 mg, 1.80 mmol) in THF (15 mL) at 0 °C. The mixture was stirred for 15 min and treated with a solution of 3-chloro-1-cyclohexene (0.39 g, 3.42 mmol) in THF (5 mL). The resulting mixture was refluxed for overnight and quenched with water. The layers were separated and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic extracts were washed (brine), dried (MgSO₄), and concentrated under vacuum. Column chromatography of the residue (SiO₂; hexanes–EtOAc = 5:1) gave compound **4** (250 mg, 41%) as a pale yellow oil. TLC (hexanes–EtOAc = 2:1): *R_f* = 0.60. ¹H NMR: δ 7.52 (br d, *J* = 7.6 Hz, 1 H), 7.26 (br d, *J* = 8.0 Hz, 1 H), 7.17 (br t, *J* = 7.6 Hz, 1 H), 7.07 (br t, *J* = 7.6 Hz, 1 H), 6.29 (s, 1 H), 5.76 (s, 2 H), 3.68 (s, 6 H), 3.64 (s, 3 H), 3.52 (d, *J* = 15.6 Hz, 1 H), 3.44 (d, *J* = 16.0 Hz, 1 H), 3.20-3.17 (m, 1 H), 2.00-1.97 (m, 2 H), 1.83-1.79 (m, 2 H), 1.60-1.38 (m, 2 H). ¹³C{¹H} NMR: δ 171.4, 171.1, 137.4, 135.8, 129.4, 128.1, 127.9, 121.3, 120.4, 119.7, 109.3, 101.3, 61.8, 52.7, 52.5, 40.2, 30.0, 29.2, 25.2, 24.9, 22.6. IR (neat, cm⁻¹): 2948, 1731, 1539, 1470, 1434, 1226. HRMS calcd (found) for C₂₁H₂₅NO₄ (M⁺): 355.1784 (355.1782).

2-(2,2-Dicarbomethoxy-4-pentenyl)-1-methyl-1*H*-indole (7, Table 1, entry 10). *n*-BuLi (2.5 M solution in hexanes, 4.2 mL, 10.5 mmol) was added to a solution of **S2** (1.61 g, 10.0 mmol) in THF (10 mL) at –78 °C. After stirring for 2 min, MsCl (1.24 g, 11.0 mmol) and LiBr (2.61 g, 30.0 mmol) were added sequentially. The resulting mixture was warmed to 0 °C, stirred for 30 min, and transferred via cannula to a solution of sodium dimethyl allylmalonate [generated from dimethyl allylmalonate (1.81 g, 10.5 mmol) and NaH (0.264 g, 11.0 mmol) in THF (20 mL)]. The reaction mixture was stirred at room temperature for 2 h and quenched with water. The layers were separated and the aqueous layer was extracted with ether (3 × 30 mL). The combined organic extracts were washed (brine), dried (MgSO₄), and concentrated under vacuum. Column chromatography of the residue (SiO₂; hexanes–EtOAc = 5:1) gave **7**

(1.90 g, 60%) as a viscous yellow oil. TLC (hexanes–EtOAc = 2:1): R_f = 0.62. ^1H NMR: δ 7.54 (br d, J = 8.0 Hz, 1 H), 7.28 (br d, J = 7.6 Hz, 1 H), 7.20 (dt, J = 1.2, 8.0 Hz, 1 H), 7.11–7.07 (m, 1 H), 6.27 (d, J = 0.8 Hz, 1 H), 5.91 (tdd, J = 7.2, 10.4, 17.2 Hz, 1 H), 5.16–5.08 (m, 2 H), 3.74 (s, 6 H), 3.67 (s, 3 H), 3.44 (s, 2 H), 2.81 (d, J = 6.8 Hz, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 171.4, 137.5, 134.9, 132.6, 128.0, 121.4, 120.4, 119.8, 109.4, 101.3, 58.2, 53.0, 37.2, 30.0, 29.5. IR (neat, cm^{-1}): 1736, 1217, 749. Anal. calcd (found) for $\text{C}_{18}\text{H}_{21}\text{NO}_4$: C, 68.55 (68.50); H, 6.71 (6.71).

2-(2-Carbomethoxy-4-pentenyl)-1-methyl-1*H*-indole (Table 1, entry 11). Compound 7 (1.01 g, 2.7 mmol) and water (0.3 mL) were added sequentially to a suspension of NaCl (0.24 g, 4.1 mmol) in DMSO (10 mL). The resulting mixture was refluxed for 2 h and then poured into brine (20 mL). The layers were separated and the aqueous layer was extracted with hexanes (5 $\times$ 15 mL). The combined organic extracts were dried (MgSO_4) and concentrated under vacuum. Column chromatography of the residue (SiO_2 ; hexanes–EtOAc = 10:1) gave 2-(2-carbomethoxy-4-pentenyl)-1-methyl-1*H*-indole (0.54 g, 73%) as a pale yellow solid. mp 63–64 $^\circ\text{C}$. TLC (hexanes–EtOAc = 2:1): R_f = 0.64. ^1H NMR: δ 7.54 (br d, J = 8.0 Hz, 1 H), 7.28 (br d, J = 8.0 Hz, 1 H), 7.18 (dt, J = 1.2, 8.0 Hz, 1 H), 7.08 (dt, J = 1.2, 7.8 Hz, 1 H), 6.29 (s, 1 H), 5.79 (tdd, J = 6.8, 10.4, 17.2 Hz, 1 H), 5.15–5.08 (m, 2 H), 3.69 (s, 3 H), 3.66 (s, 3 H), 3.18–3.11 (m, 1 H), 2.95–2.87 (m, 2 H), 2.53–2.37 (m, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 175.4, 138.2, 137.7, 135.1, 128.1, 121.2, 120.3, 119.7, 117.9, 109.2, 100.3, 52.1, 45.1, 36.7, 29.9, 28.8. IR (neat, cm^{-1}): 2948, 1737, 1468, 919, 748. HRMS calcd (found) for $\text{C}_{16}\text{H}_{19}\text{NO}_2$ (M^+): 257.1416 (257.1418).

***N*-Allyl-*N*-methyl 1-methyl-1*H*-indole-2-carboxamide (Table 1, entry 12).** Oxallyl chloride (3.81 g, 30.0 mmol) and DMF (0.5 mL) were added to a solution of 1-methyl-1*H*-indole-2-carboxylic acid (1.75 g, 10.0 mmol) in CH_2Cl_2 (100 mL). The resulting mixture was refluxed for 1 h and then concentrated under vacuum. The residue was dissolved in CH_2Cl_2

(100 mL) and treated with *N*-methyl allylamine (2.87 mL, 30.0 mmol) at 0 °C. The resulting mixture was stirred for 1 h at room temperature and then quenched with 1N HCl. The layers were separated and the aqueous layer was extracted with ether (3 × 100 mL). The combined organic extracts were washed (brine), dried (MgSO₄), and concentrated under vacuum. Column chromatography of the residue (SiO₂; hexanes–EtOAc = 3:1) gave *N*-allyl-*N*-methyl 1-methyl-1*H*-indole-2-carboxamide (1.92 g, 84%) as a yellow oil. TLC (hexanes–EtOAc = 2:1): *R_f* = 0.32. ¹H NMR: δ 7.63 (br d, *J* = 8.0 Hz, 1 H), 7.37 (dd, *J* = 0.8, 8.2 Hz, 1 H), 7.30 (dt, *J* = 1.0, 7.0 Hz, 1 H), 7.15 (dt, *J* = 1.0, 7.2 Hz, 1 H), 6.69 (br s, 1 H), 5.86 (br s, 1 H), 5.35–5.28 (m, 2 H), 4.18 (d, *J* = 2.8 Hz, 2 H), 3.86 (s, 3 H), 3.13 (s, 3 H). ¹³C{¹H} NMR: δ 164.3, 138.2, 133.4, 132.1, 126.7, 123.6, 121.5, 120.4, 117.8, 110.1, 103.4, 54.2, 37.2, 31.4. IR (neat, cm⁻¹): 3060, 1640, 1598, 1504, 1230, 920, 748. Anal. calcd (found) for C₁₄H₁₆N₂O: C, 73.66 (73.56); H, 7.06 (6.96).

2-(1,1-Dimethyl-3-butenyl)-1-methyl-1*H*-indole (Table 1, entry 14). 2-(1,1-Dimethyl-3-butenyl)-1*H*-indole (**S8**) was isolated in 41% yield as a yellow oil from reaction of **S1** and methyl 2,2-dimethyl-4-pentenoate employing a procedure similar to that used to synthesize **S4**. 2-(1,1-Dimethyl-3-butenyl)-1-methyl-1*H*-indole was isolated in 55% yield as a yellow oil from reaction of **S8** and methyl iodide employing a procedure similar to that used to synthesize **1**.

For S8: TLC (hexanes–CH₂Cl₂ = 1:1): *R_f* = 0.56. ¹H NMR: δ 7.98 (s, 1 H), 7.60–7.57 (m, 1 H), 7.36–7.33 (m, 1 H), 7.19–7.09 (m, 2 H), 6.30 (dd, *J* = 0.8, 2.0 Hz, 1 H), 5.71 (tdd, *J* = 6.4, 10.2, 17.0 Hz, 1 H), 5.11–5.05 (m, 2 H), 2.42 (td, *J* = 1.0, 7.6 Hz, 2 H), 1.40 (s, 6 H). ¹³C{¹H} NMR: δ 147.4, 136.1, 135.2, 128.7, 121.4, 120.3, 119.9, 118.0, 110.7, 98.5, 48.1, 35.3, 28.0. IR (neat, cm⁻¹): 3422, 2965, 1458, 1295, 914, 784, 749, 698. Anal. calcd (found) for C₁₄H₁₇N: C, 84.37 (84.50); H, 8.60 (8.60).

For 2-(1,1-Dimethyl-3-butenyl)-1-methyl-1*H*-indole: TLC (hexanes–CH₂Cl₂ =

5:1): R_f = 0.44. ^1H NMR: δ 7.61-7.59 (m, 1 H), 7.33 (br d, J = 8.0, 1 H), 7.25-7.21 (m, 1 H), 7.15-7.11 (m, 1 H), 6.36 (m, 1 H), 5.64 (tdd, J = 6.4, 10.2, 17.0 Hz, 1 H), 5.12-5.00 (m, 2 H), 3.93 (s, 3 H), 2.61 (dd, J = 0.8, 7.2 Hz, 2 H), 1.51 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 147.6, 139.0, 135.2, 127.5, 121.2, 120.3, 119.6, 117.5, 108.9, 100.1, 46.2, 35.9, 32.7, 28.6. IR (neat, cm^{-1}): 2978, 1468, 1354, 1314, 913, 780, 749, 732. Anal. calcd (found) for $\text{C}_{15}\text{H}_{19}\text{N}$: C, 84.46 (84.43); H, 8.98 (8.96).

2-(3-Butenyl)-1-methyl-1*H*-indole (Table 1, entry 15). 2-(3-Butenyl)-1-methyl-1*H*-indole was isolated in 76% yield as a yellow oil from reaction of 2-(3-butenyl)-1*H*-indole and methyl iodide employing a procedure similar to that used to synthesize **1**. TLC (hexanes– CH_2Cl_2 = 5:1): R_f = 0.67. ^1H NMR: δ 7.60 (br d, J = 7.6 Hz, 1 H), 7.32 (dd, J = 0.8, 8.0 Hz, 1 H), 7.22 (ddd, J = 1.2, 7.6, 8.0 Hz, 1 H), 7.14 (dt, J = 1.2, 7.8 Hz, 1 H), 6.34-6.33 (m, 1 H), 6.00 (tdd, J = 6.8, 10.4, 17.2 Hz, H), 5.23-5.10 (m, 2 H), 3.71 (s, 3 H), 2.89 (t, J = 7.6 Hz, 2 H), 2.59-2.53 (m, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 140.8, 137.9, 137.7, 128.2, 120.9, 120.1, 119.6, 115.7, 109.0, 99.1, 32.9, 29.7, 26.7. IR (neat, cm^{-1}): 3058, 2928, 1460, 1312, 933, 772. Anal. calcd (found) for $\text{C}_{13}\text{H}_{15}\text{N}$: C, 84.28 (84.18); H, 8.16 (8.29).

Dimethyl 2-(1,3-dideuterio-2-cyclohexenyl)-2-(1-methyl-1*H*-indol-2-ylmethyl)malonate (4-*d*₂**).** Triethylamine (12.9 mL, 90 mmol) and acetylchloride (3.51 g, 45.0 mmol) were added sequentially to a solution of 1,3-dideuterio-2-cyclohexen-1-ol (3.00 g, 30.0 mmol) in ether (150 mL) at 0 °C. The resulting mixture was stirred at room temperature overnight and quenched with saturated aqueous NH_4Cl . The layers were separated and the aqueous layer was extracted with ether (3 $\times$ 100 mL). The combined organic extracts were washed (brine), dried (MgSO_4), and concentrated to give 1,3-dideuterio-2-cyclohexenyl acetate (**S9-*d*₂**) (3.87 g, 87%) as a colorless oil. Compound **S9-*d*₂** was used for next step without further purification. Triphenylphosphine (371 mg, 1.42 mmol), $\text{Pd}(\text{OAc})_2$ (115 mg, 0.47 mmol), and **S9-*d*₂** (1.86 g, 11.8 mmol)

were added sequentially to a solution of sodium dimethyl malonate [generated from dimethyl malonate (2.34 g, 17.7 mmol) and NaH (0.45 g, 18.6 mmol) in THF (55 mL)] at 0 °C. The resulting mixture was refluxed overnight and quenched with saturated aqueous NH_4Cl . The layers were separated and the aqueous layer was extracted with ether (3×50 mL). The combined organic extracts were dried (MgSO_4) and concentrated under vacuum. Column chromatography of the residue (SiO_2 ; hexanes–EtOAc = 5:1) gave dimethyl 2-(1,3-deuterium-2-cyclohexenyl)malonate (**S10- d_2**) (2.48 g, 98%) as a yellow oil. Compound **4- d_2** was isolated in 76% yield as a viscous yellow oil from reaction of **S2** and **S10- d_2** employing a procedure similar to that used to synthesize **7**.

For S9- d_2 : TLC (hexanes–EtOAc = 2:1): R_f = 0.76. ^1H NMR: δ 5.66 (br s, 1 H), 2.00 (s, 3 H), 2.00–1.57 (m, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 171.0, 132.6 (t, J = 24.1 Hz), 125.7, 67.9 (t, J = 22.8 Hz), 28.4, 25.0, 21.6, 19.0. HRMS calcd (found) for $\text{C}_8\text{H}_{10}\text{D}_2\text{O}_2$ (M^+): 142.0961 (142.0965).

For S10- d_2 : TLC (hexanes–EtOAc = 2:1): R_f = 0.61. ^1H NMR: δ 5.49 (br s, 1 H), 3.71 (s, 3 H), 3.70 (s, 3 H), 3.25 (s, 1 H), 1.97–1.94 (m, 2 H), 1.77–1.64 (m, 2 H), 1.57–1.49 (m, 1 H), 1.37–1.30 (m, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 169.1, 169.1, 129.7 (t, J = 23.7 Hz), 127.4, 57.0, 52.6, 35.2 (t, J = 20.2 Hz), 26.8, 25.1, 21.1. HRMS calcd (found) for $\text{C}_{11}\text{H}_{14}\text{D}_2\text{O}_4$ (M^+): 214.1172 (214.1173).

For 4- d_2 : TLC (hexanes–EtOAc = 2:1): R_f = 0.60. ^1H NMR: δ 7.52 (br d, J = 7.6 Hz, 1 H), 7.26 (br d, J = 8.0 Hz, 1 H), 7.17 (br t, J = 7.6 Hz, 1 H), 7.07 (br t, J = 7.6 Hz, 1 H), 6.29 (s, 1 H), 5.76 (br s, 1 H), 3.69 (s, 3 H), 3.67 (s, 3 H), 3.65 (s, 3 H), 3.52 (d, J = 16.4 Hz, 1 H), 3.46 (d, J = 15.8 Hz, 1 H), 2.00–1.95 (m, 2 H), 1.85–1.80 (m, 2 H), 1.62–1.41 (m, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 171.4, 171.1, 137.4, 135.8, 129.1 (t, J = 23.8 Hz), 128.1, 127.6, 121.3, 120.4, 119.7, 109.3, 101.3, 61.8, 52.7, 52.5, 39.7 (t, J = 22.0 Hz), 30.0, 29.2, 25.2, 24.9, 22.6. HRMS calcd (found) for $\text{C}_{21}\text{H}_{23}\text{D}_2\text{NO}_4$ (M^+): 357.1907 (355.1912).

Cyclization of 2-Alkenyl Indoles

Table S1. Effect of Pt(II) source, catalyst loading, acid concentration, solvent, temperature, and time on the platinum-catalyzed cyclization of **1**.

entry	Pt(II) source	cat loading (mol% Pt)	HCl (mol%)	solvent	solvent vol. (mL)	temp (°C)	time (h)	product ratio (1:2:3) ^a
1	[PtCl ₂ (H ₂ C=CH ₂)] ₂	5	0	dioxane	2	90	12	13:67:13
2	[PtCl ₂ (H ₂ C=CH ₂)] ₂	5	10	dioxane	2	90	12	<1:83:14
3	[PtCl ₂ (H ₂ C=CH ₂)] ₂	5	5	dioxane	2	90	12	<1:85:11
4	[PtCl ₂ (H ₂ C=CH ₂)] ₂	5	5	dioxane	2	60	24	<1:85:4
5	[PtCl ₂ (H ₂ C=CH ₂)] ₂	2	5	dioxane	1	60	24	<1:92:4
6	PtCl ₂	2	5	dioxane	1	60	24	<1:96:2
7	PtCl ₂ (MeCN) ₂	2	5	dioxane	1	60	24	<1:80:15
8	PtCl ₂	2	1	dioxane	1	60	24	<1:90:5
9	PtCl ₂	2	5	THF	1	60	24	8:79:4
10	PtCl ₂	2	5	DCE	1	60	24	2:93:3
11	PtCl ₂	2	5	toluene	1	60	24	40:57: <1
12	none	0	30	dioxane	1	60	24	92:<1:<1

^aAs determined by GC analysis of the crude reaction mixture.

4,9-Dimethyl-2,3,4,9-tetrahydro-1H-carbazole (2). A solution of 1-methyl-2-(4-pentenyl)indole (**1**) (97 mg, 0.50 mmol), PtCl₂ (2.7 mg, 0.010 mmol), and HCl (4.0 M solution in dioxane, 6.5 μL, 0.025 mmol) was stirred at 60 °C for 18 h, cooled to room temperature, and quenched with 1N aqueous NaOH. The layers were separated and the aqueous layer was extracted with ether (3 × 2 mL). The combined organic extracts were washed (brine)

and concentrated under vacuum. Column chromatography of the residue (SiO₂; hexanes-CH₂Cl₂ = 5:1) gave **2** (89 mg, 92%) as a colorless oil. TLC (hexanes-CH₂Cl₂ = 5:1): *R_f* = 0.37. ¹H NMR: δ 7.64 (br d, *J* = 7.6 Hz, 1 H), 7.32-7.29 (m, 1 H), 7.19 (dt, *J* = 1.6, 7.6 Hz, 1 H), 7.12 (dt, *J* = 1.2, 7.4 Hz, 1 H), 3.65 (s, 3H), 3.22-3.14 (m, 1 H), 2.72 (dq, *J* = 0.8, 6.2 Hz, 2 H), 2.09-1.97 (m, 2 H), 1.94-1.88 (m, 2 H), 1.66-1.60 (m, 1 H), 1.43 (d, *J* = 6.8 Hz, 3 H). ¹³C{¹H} NMR: δ 137.2, 135.7, 127.0, 120.6, 118.9, 118.8, 114.5, 108.9, 32.3, 29.2, 27.5, 22.6, 21.8, 20.6. IR (neat, cm⁻¹): 3051, 2927, 2857, 1470, 1375, 1313, 1244. HRMS calcd (found) for C₁₄H₁₇N (M⁺): 199.1361 (199.1362).

All remaining polycyclic indole derivatives were isolated from the corresponding 2-alkenylindoles employing a similar procedure to that for the synthesis of **2** unless noted otherwise.

4,9-Dimethy-9H-carbazole (3).⁸ Compound **3** was isolated in 88% yield as a white solid from dehydrogenation of **2** (Pd/C) employing a published procedure.⁹ ¹H NMR: δ 8.30-8.27 (m, 1 H), 7.58-7.54 (m, 1 H), 7.48-7.44 (m, 1 H), 7.36-7.31 (m, 2 H), 7.12-7.10 (m, 1 H), 3.86 (s, 3H), 2.98 (s, 3 H). ¹³C{¹H} NMR: δ 141.3, 141.2, 133.7, 125.8, 125.3, 123.7, 122.7, 121.6, 120.8, 119.1, 108.5, 106.3, 29.3, 21.1.

9-Benzyl-4-methyl-2,3,4,9-tetrahydro-1H-carbazole (Table 1, entry 2).¹⁰ ¹H NMR: δ 7.73-7.69 (m, 1 H), 7.36-7.27 (m, 5 H), 7.24-7.14 (m, 2 H), 7.09-7.07 (m, 2 H), 5.30 (s, 2H), 3.31-3.23 (m, 1 H), 2.70 (dq, *J* = 0.8, 6.2 Hz, 2 H), 2.11-1.97 (m, 2 H), 1.93-1.86 (m, 2 H), 1.73-1.65 (m, 1 H), 1.50 (d, *J* = 7.2 Hz, 3 H). ¹³C{¹H} NMR: δ 138.6, 137.1, 135.6, 129.0, 127.5, 126.5, 120.9, 119.1, 119.0, 115.1, 109.4, 46.5, 32.2, 27.5, 22.6, 21.8, 20.6.

6-Methoxy-4,9-dimethyl-2,3,4,9-tetrahydro-1H-carbazole (Table 1, entry 3). Yellow oil, 88%. TLC (hexanes-CH₂Cl₂ = 1:2): *R_f* = 0.66. ¹H NMR: δ 7.19 (d, *J* = 8.8 Hz, 1 H), 7.11 (d, *J* = 2.4 Hz, 1 H), 6.88 (dd, *J* = 2.4, 8.8 Hz, 1 H), 3.93 (s, 3 H), 3.61 (s, 3 H),

3.21-3.13 (m, 1 H), 2.78-2.64 (m, 2 H), 2.11-1.97 (m, 3 H), 1.67-1.61 (m, 1 H), 1.43 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 153.8, 136.5, 132.6, 127.3, 114.1, 110.0, 109.4, 101.7, 56.4, 32.2, 29.3, 27.4, 22.7, 21.5, 20.5. IR (neat, cm^{-1}): 2930, 1485, 1151, 1036, 792. HRMS calcd (found) for $\text{C}_{15}\text{H}_{19}\text{NO}$ (M^+): 229.1467 (229.1471).

2,2-Dicarbomethoxy-9-methyl-4-propyl-1,3,4,9-tetrahydrocarbazole (Table 1, entries 4 and 5). Viscous colorless oil, 80%. TLC (hexanes-EtOAc = 2:1): $R_f = 0.57$. ^1H NMR: δ 7.61 (br d, $J = 8.0$ Hz, 1 H), 7.29 (br d, $J = 8.4$ Hz, 1 H), 7.19 (dt, $J = 0.8, 7.2$ Hz, 1 H), 7.09 (dt, $J = 0.8, 7.4$ Hz, 1 H), 3.83 (s, 3 H), 3.68 (s, 3 H), 3.67 (s, 3 H), 3.51 (d, $J = 16.0$ Hz, 1 H), 3.25-3.19 (m, 1 H), 3.15 (dd, $J = 2.2, 15.8$ Hz, 1 H), 2.79 (ddd, $J = 2.2, 5.8, 13.2$ Hz, 1 H), 2.25-2.17 (m, 1 H), 1.95 (dd, $J = 10.4, 13.2$ Hz, 1 H), 1.63-1.42 (m, 3 H), 1.01 (t, $J = 7.2$ Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 172.7, 171.1, 137.8, 132.9, 126.5, 120.9, 119.7, 118.9, 111.8, 109.1, 54.8, 53.2, 53.1, 37.6, 35.4, 31.0, 29.5, 28.5, 19.6, 14.6. IR (neat, cm^{-1}): 2949, 2871, 1730, 1469, 1380, 1236, 1236, 740. Anal. calcd (found) for $\text{C}_{20}\text{H}_{25}\text{NO}_4$: C, 69.95 (69.82); H, 7.34 (7.34).

4,4,9-Trimethyl-2,3,4,9-tetrahydro-1H-carbazole (Table 1, entry 6). White solid, 91%. mp 62-64 °C. TLC (hexanes- CH_2Cl_2 = 5:1): $R_f = 0.38$. ^1H NMR: δ 7.73 (br d, $J = 8.0$ Hz, 1 H), 7.31-7.28 (m, 1 H), 7.18 (dt, $J = 1.2, 7.6$ Hz, 1 H), 7.10 (dt, $J = 1.2, 7.4$ Hz, 1 H), 3.63 (s, 3H), 2.71 (t, $J = 6.2$ Hz, 2 H), 2.00-1.94 (m, 2 H), 1.74-1.71 (m, 2 H), 1.49 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 137.3, 135.1, 126.1, 120.4, 120.1, 118.6, 117.7, 109.0, 40.7, 32.2, 29.9, 29.3, 22.8, 20.2. IR (neat, cm^{-1}): 2923, 1464. Anal. calcd (found) for $\text{C}_{15}\text{H}_{19}\text{N}$: C, 84.46 (84.43); H, 8.98 (9.12).

1,1,4,9-Tetramethyl-2,3,4,9-tetrahydro-1H-carbazole (Table 1, entry 7). Colorless oil, 91%. TLC (hexanes- CH_2Cl_2 = 5:1): $R_f = 0.40$. ^1H NMR: δ 7.66-7.64 (m, 1 H), 7.33 (br d, $J = 8.0$ Hz, 1 H), 7.19 (dt, $J = 1.2, 7.6$ Hz, 1 H), 7.12 (dt, $J = 1.2, 7.4$ Hz, 1 H), 3.87 (s,

3H), 3.25-3.17 (m, 1 H), 2.13-2.05 (m, 1 H), 2.00-1.99 (m, 1 H), 1.71-1.62 (m, 2 H), 1.54 (s, 3 H), 1.46 (s, 3 H), 1.44 (d, $J = 7.2$ Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 142.0, 138.0, 126.7, 121.1, 119.1, 118.9, 114.4, 108.9, 39.3, 32.6, 32.2, 29.1, 28.8, 28.2, 27.8, 21.6. IR (neat, cm^{-1}): 2959, 2920, 1470, 1360, 738. Anal. calcd (found) for $\text{C}_{16}\text{H}_{21}\text{N}$: C, 84.53 (84.37); H, 9.31 (9.60).

1,1,4-Trimethyl-2,3,4,9-tetrahydro-1H-carbazole (Table 1, entry 8). White solid, 87%. mp 91-94 °C. TLC (hexanes- $\text{CH}_2\text{Cl}_2 = 1:1$): $R_f = 0.64$. ^1H NMR: δ 7.71 (s, 1 H), 7.60 (br d, $J = 8.0$, 1 H), 7.337.31 (m, 1 H), 7.17-7.08 (m, 1 H), 3.15-3.10 (m, 1 H), 2.10-2.03 (m, 1 H), 1.89-1.81 (m, 1 H), 1.69-1.59 (m, 2 H), 1.39 (d, $J = 7.2$ Hz, 3 H), 1.36 (s, 3 H), 1.32 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 141.7, 136.2, 127.6, 121.2, 119.9, 119.3, 114.0, 110.9, 36.5, 31.8, 29.7, 29.4, 29.2, 27.7, 21.6. IR (neat, cm^{-1}): 3417, 2957, 2924, 2867, 1450, 745. Anal. calcd (found) for $\text{C}_{15}\text{H}_{19}\text{N}$: C, 84.46 (84.31); H, 8.98 (8.76).

cis-5,5-Dicarbomethoxy-7-methyl-2,3,4a,6,7,11c-hexahydro-1H,4H-benzo[c]carbazole (5). White solid, 82%. mp 165-166 °C. TLC (hexanes-EtOAc = 2:1): $R_f = 0.55$. ^1H NMR: δ 7.67 (d, $J = 8.0$ Hz, 1 H), 7.29 (d, $J = 8.0$ Hz, 1 H), 7.17 (dt, $J = 1.2$, 7.6 Hz, 1 H), 7.06 (dt, $J = 1.2$, 7.6 Hz, 1 H), 3.82 (s, 3 H), 3.70 (s, 3 H), 3.68 (s, 3 H), 3.55 (d, $J = 17.2$ Hz, 1 H), 3.44-3.42 (br s, 1 H), 3.19 (dd, $J = 2.8$, 17.6 Hz, 1 H), 2.87 (br d, $J = 14.4$ Hz, 1 H), 2.83 (td, $J = 4.0$, 12.0, 2 H), 1.78 (tt, $J = 3.8$, 13.6 Hz, 1 H), 1.66-1.63 (m, 1 H), 1.50-1.45 (m, 2 H), 1.39 (tq, $J = 3.2$, 12.8 Hz, 1 H), 1.28 (dq, $J = 4.0$, 12.8 Hz, 1 H), 1.14 (tq, $J = 3.2$, 13.2 Hz, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 171.2, 170.8, 137.9, 133.4, 126.8, 120.7, 119.9, 119.0, 109.0, 108.9, 59.5, 53.4, 53.3, 41.3, 32.6, 29.7, 26.3, 24.6, 24.2, 21.5. IR (neat, cm^{-1}): 2932, 2854, 1742, 1469, 1237, 737. Anal. calcd (found) for $\text{C}_{21}\text{H}_{25}\text{NO}_4$: C, 70.96 (70.82); H, 7.09 (7.23). The cis stereochemistry of **5** was determined by single crystal X-ray analysis (see below).

2,2-Dicarbomethoxy-4,9-dimethyl-1,3,4,9-tetrahydrocarbazole (8). White solid, 90%. mp 127-129 °C. TLC (hexanes-EtOAc = 2:1): R_f = 0.54. ^1H NMR: δ 7.61 (br d, J = 7.6 Hz, 1 H), 7.30-7.27 (m, 1 H), 7.18 (dt, J = 1.2, 7.2 Hz, 1 H), 7.07 (dt, J = 1.2, 7.4 Hz, 1 H), 3.82 (s, 3H), 3.68 (s, 3 H), 3.67 (s, 3 H), 3.53 (td, J = 1.4, 16.0 Hz, 1 H), 3.22-3.17 (m, 1 H), 3.12 (dd, J = 2.4, 16.4 Hz, 1 H), 2.72 (ddd, J = 1.8, 6.4, 13.2 Hz, 1 H), 1.88 (dd, J = 10.4, 13.6 Hz, 1 H), 1.47 (d, J = 6.8 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 172.6, 171.1, 137.8, 132.5, 126.5, 121.0, 119.7, 119.0, 112.8, 109.1, 54.8, 53.3, 53.1, 38.7, 29.5, 28.5, 26.4, 21.6. IR (neat, cm^{-1}): 2948, 1735, 1465, 1247, 1200, 740. Anal. calcd (found) for $\text{C}_{18}\text{H}_{21}\text{NO}_4$: C, 68.55 (68.57); H, 6.71 (6.73).

2-Carbomethoxy-4,9-dimethyl-1,3,4,9-tetrahydrocarbazole (Table 1, entry 11). Pale yellow oil, 98%. TLC (hexanes-EtOAc = 2:1): R_f = 0.60. ^1H NMR (major diastereomer): δ 7.58 (br d, J = 7.6 Hz, 1 H), 7.33-7.30 (m, 1 H), 7.20 (dt, J = 1.2, 7.2 Hz, 1 H), 7.15-7.11 (m, 1 H), 3.81 (s, 3 H), 3.66 (s, 3 H), 3.36-3.32 (m, 1 H), 3.14-2.85 (m, 3 H), 2.17-2.06 (m, 2 H), 1.42 (d, J = 6.8 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 176.3, 137.5, 133.5, 126.5, 121.1, 119.8, 119.0, 113.9, 109.0, 52.5, 40.7, 36.6, 34.1, 29.2, 26.1, 25.0. IR (neat, cm^{-1}): 2958, 1730, 1470, 1379, 1014, 739. HRMS calcd (found) for $\text{C}_{16}\text{H}_{19}\text{NO}_2$ (M^+): 257.1416 (257.1407).

2,4,9-Trimethyl-2,3,4,9-tetrahydro- β -1-carbolinone (Table 1, entry 12). White solid, 80%. mp 67-69 °C. TLC (hexanes-EtOAc = 2:1): R_f = 0.32. ^1H NMR: δ 7.65 (br d, J = 8.0 Hz, 1 H), 7.38-7.31 (m, 2 H), 7.14 (dt, J = 1.2, 7.2 Hz, 1 H), 4.13 (s, 3 H), 3.78 (dd, J = 5.0, 11.8 Hz, 1 H), 3.38-3.29 (m, 2 H), 3.15 (s, 3 H), 1.41 (d, J = 6.8 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 162.0, 139.4, 125.9, 124.6, 123.8, 123.6, 120.6, 120.2, 110.6, 57.1, 34.7, 31.4, 27.5, 19.0. IR (neat, cm^{-1}): 2968, 2924, 1645, 1540, 1493, 1396, 1373, 1326, 741. Anal. calcd (found) for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$: C, 73.66 (73.60); H, 7.06 (6.96).

2,4-Dimethyl-2,3,4,9-tetrahydro- β -1-carbolinone (Table 1, entry 13). White

solid, 82%. mp 212-214 °C. TLC (hexanes-EtOAc = 1:2): R_f = 0.36. ^1H NMR: δ 11.12 (s, 1 H), 7.67 (br d, J = 8.0 Hz, 1 H), 7.60 (br d, J = 8.0 Hz, 1 H), 7.32 (br t, J = 7.6 Hz, 1 H), 7.15 (br t, J = 7.2 Hz, 1 H), 3.78 (dd, J = 5.2, 11.6 Hz, 1 H), 3.45-3.34 (m, 2 H), 3.25 (s, 3 H), 1.44 (d, J = 6.8 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 162.1, 138.3, 126.5, 125.1, 124.6, 122.9, 120.5, 120.1, 113.3, 57.5, 34.6, 27.7, 18.9. IR (neat, cm^{-1}): 3190, 1631, 1548, 1401, 1325, 780, 733. HRMS calcd (found) for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}$ (M^+): 214.1106 (214.1102).

1,1,9-Trimethyl-2,3,4,9-tetrahydro-1H-carbazole (Table 1, entry 14).¹¹ White solid, 89%. TLC (hexanes- CH_2Cl_2 = 5:1): R_f = 0.40. ^1H NMR: δ 7.51 (br d, J = 8.0 Hz, 1 H), 7.29 (br d, J = 8.0, 1 H), 7.22 (dt, J = 1.2, 7.2 Hz, 1 H), 7.12 (dt, J = 1.2, 7.2 Hz, 1 H), 3.85 (s, 3H), 2.76 (t, J = 6.2 Hz, 2 H), 1.92-1.88 (m, 2 H), 1.81-1.78 (m, 2 H), 1.47 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 142.4, 137.8, 127.1, 121.2, 119.0, 118.4, 109.5, 108.7, 43.1, 32.7, 32.2, 28.7, 22.4, 20.7.

9-Methyl-2,3,4,9-tetrahydro-1H-carbazole (Table 1, entry 15).¹² White solid, 74%. ^1H NMR: δ 7.51 (br d, J = 7.6 Hz, 1 H), 7.30-7.27 (m, 1 H), 7.19 (dt, J = 1.2, 7.6 Hz, 1 H), 7.12 (dt, J = 1.2, 7.4 Hz, 1 H), 3.64 (s, 3H), 2.79-2.73 (m, 2 H), 2.01-1.87 (m, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 137.0, 136.0, 127.5, 120.8, 118.9, 118.0, 109.5, 108.8, 29.2, 23.6, 22.4, 21.4.

***anti*-5,5-Dicarbomethoxy-1,4a-dideuterio-7-methyl-2,3,4a,6,7,11c-hexahydro-1H,4H-benzo[c]carbazole (*anti*-5- d_2).** White solid, 73%. TLC (hexanes-EtOAc = 2:1): R_f = 0.55. The ^1H and ^{13}C resonances of *anti*-5- d_2 were assigned from the two-dimensional COSY (Figures S1 and S2), HMQC (Figure S3 and S4), and HMBC (Figures S5 and S6) correlation spectra and from selective decoupling of the one dimensional 800 MHz ^1H NMR spectrum. The numbering scheme for the ^1H and ^{13}C resonances of *anti*-5- d_2 are provided in Figure S7. ^1H NMR (800 MHz): δ 7.69 (d, J = 8.0 Hz, 1 H, H_6), 7.31 (d, J = 8.0 Hz, 1 H, H_4), 7.19 (dt, J = 1.2, 7.6 Hz, 1 H, H_5), 7.08 (dt, J = 1.2, 7.6 Hz, 1 H, H_3), 3.84 (s, 3 H, H_{22}/H_{26}), 3.72 (s,

3 H, H_9), 3.70 (s, 3 H, H_{26}/H_{20}), 3.59 (dd, $J = 1.2, 16.8$ Hz, 1 H, H_{11}), 3.45 (br s, 1 H, H_{14}),
 3.22 (dd, $J = 1.4, 16.8$ Hz, 1 H, H_{11}), 1.78 (ddd, $J = 3.2, 4.2, 13.8$ Hz, 1 H, H_{15ax}), 1.67 (pt, $J =$
 3.2, 12.8, 1 H, H_{17eq}), 1.53-1.48 (m, 2 H, $H_{16eq}H_{18eq}$), 1.41 (tq, $J = 3.6, 12.8$ Hz, 1 H, H_{17ax}),
 1.29 (dt, $J = 4.0, 12.8$ Hz, 1 H, H_{18ax}), 1.17 (ddt, $J = 3.2, 12.8, 13.8$ Hz, 1 H, H_{16ax}). $^{13}\text{C}\{^1\text{H}\}$
 NMR (800 MHz): δ 171.1 (C_{19}/C_{23}), 170.7 (C_{23}/C_{19}), 137.8 (C_7), 133.3 (C_{10}), 126.7 (C_2),
 120.7 (C_5), 119.8 (C_6), 118.9 (C_3), 109.0 (C_4), 108.9 (C_1), 59.3 (C_{12}), 53.3 (C_{22}/C_{26}), 53.2
 (C_{26}/C_{22}), 40.7 (t, $J = 20.2$ Hz, C_{13}), 32.3 (C_{14}), 29.6 (C_9), 29.3 (t, $J = 21.0$ Hz, C_{15}), 26.2 (C_{16}),
 24.6 (C_{11}), 24.0 (C_{18}), 21.4 (C_{17}).

Figure S1. COSY NMR spectrum of *anti*-**5**- d_2 .

Figure S2. Partial COSY NMR spectrum of *anti*-**5**- d_2 .

Figure S3. HMQC NMR spectrum of *anti*-**5**- d_2 .

Figure S5. HMBC NMR spectrum of *anti*-5- d_2 .

Figure S6. Partial HMBC NMR spectrum of *anti*-5- d_2 .

Figure S7. Numbering scheme for the ^{13}C and ^1H resonances of *anti*-**5**- d_2 .

Stereochemical Analysis of *anti*-**5**- d_2

Key to the stereochemical analysis of *anti*-**5**- d_2 was the resonance at δ 1.78 assigned to proton $H_{15\text{ax}}$ that displayed a 3.2 Hz coupling to $H_{16\text{eq}}$, a 4.2 Hz coupling to H_{14} and a 13.8 Hz coupling to $H_{16\text{ax}}$. The large 13.8 Hz coupling between $H_{15\text{ax}}$ and $H_{16\text{ax}}$ is particularly diagnostic as this coupling constant establishes both the axial orientation of $H_{15\text{ax}}$ and $H_{16\text{ax}}$ and the static nature of the fused cyclohexane ring. This information, combined with the X-ray crystallographic analysis of **5** establishes the anti addition of the indole and platinum across the C=C bond of **4**- d_2 , provided that protonolysis of the intermediate palladium alkyl intermediate *anti*-**II**- d_2 occurs with retention of stereochemistry, as has been previously established.¹³

Asymmetric Indole Alkylation

Table S2. Effect of ligand on the yield and enantioselectivity of the conversion of **7** to **8** catalyzed by a 1:1 mixture of platinum dichloride bis(phosphine) complex (10 mol%) and AgOTf (10 mol%) in dioxane at 60 °C for 22-24 h.

P-P	yield (%)	ee (%)
(S)-BINAP	82	≤5
(R)-Tol-BINAP	86	15
(R)-3,5-xylyl-BINAP	81	35
(R)-3,5- <i>i</i> -Pr-MeOBIPHEP	86	56
(R)-3,5- <i>t</i> -Bu-4-MeO-MeOBIPHEP	84	69

(R)-6. A mixture of (*R*)-**S3** (89 mg, 0.077 mmol) and Pt(COD)Cl₂ (29 mg, 0.077 mmol) in 2.5 mL of CH₂Cl₂ was stirred at room temperature for 20 h. The resulting mixture was concentrated to ~0.5 mL under vacuum and the oily residue was treated with pentane. The resulting precipitate was collected by filtration, washed by pentane, and dried under vacuum to give (*R*)-**6** (86 mg, 79 %) as a pale yellow solid. ¹H NMR: δ 8.60-6.50 (m, 14 H), 3.68 (s, 6 H), 3.61 (s, 12 H), 1.37 (s, 72 H). ³¹P{¹H} NMR 11.4 (s, ¹J_{P-Pt} = 3664 Hz). Anal. Calcd. (found) for C₇₄H₁₀₄Cl₂O₆P₂Pt: C, 62.70 (62.56); H, 7.39 (7.52).

Cyclization of 7 catalyzed by (R)-6. A suspension of **7** (87 mg, 0.28 mmol), (*R*)-**6** (39 mg, 0.028 mmol), and AgOTf (7 mg, 0.028) in 1.2 ml of dioxane was stirred at 60 °C for 24 hours, cooled to room temperature, and filtered through a plug of silica gel, eluting with ether. The filtrate was concentrated under vacuum and the residue was

chromatographed (hexanes–EtOAc = 10:1 → 5:1) to give **8** (73 mg, 84%, 69% ee) as a white solid. The enantiomeric excess of **8** was determined by HPLC analysis using a Chiralpak AD-H column (hexanes/2-propanol = 90/10, 0.6 mL/min). The retention times for the two enantiomers was 11.6 and 13.7 min, respectively (Figure S8).

Figure S8. Chiral HPLC trace for racemic **8** (left trace) and enantiomerically enriched **8** (right trace).

X-ray Crystallography of **5**.

Crystals of **5** suitable for X-ray diffraction were obtained by slow cooling of a saturated EtOAc/hexanes (v/v $\approx$ 10/1) solution (25 $\rightarrow$ -20 $^{\circ}$ C). Tables of crystallographic and refinement data (Table S3), atomic coordinates (Table S4), bond lengths (Table S5), and bond angles (Table S6) are provided.

Figure S9. X-ray crystal structure of **5**.

Table S3. X-ray crystal data and collection and refinement of parameters for **5**.

empirical formula	$\text{C}_{21}\text{H}_{26}\text{NO}_4$
fw	355.43
crystal size (mm)	$0.35 \times 0.30 \times 0.25$
crystal system	triclinic
space group	$P\bar{1}$
a (Å)	7.9313(2)
b (Å)	9.1118(2)
c (Å)	12.8139(3)
α (deg)	74.133(1)
β (deg)	87.125(1)
γ (deg)	89.691(1)
V (Å ³)	889.60(4)
Z	2
scan mode	ω
2θ limits (deg)	$5.00 < 2\theta < 56.00$
D_c (mg*cm ⁻³)	1.327
abs coeff (mm ⁻¹)	0.09
unique reflections	4282
data with $I_{\text{net}} > 2.5\sigma(I)$	3183
$F(000)$	380.24
R_f	0.041
R_w	0.047
GoF	1.7665
No. of parameters	336
max Δ/σ	0.000
largest resid density (e/Å ³)	0.340

Table S4. Atomic coordinates for **5**.

	x	y	z	Biso ^a
C1	0.89147(17)	0.34476(17)	0.76227(11)	1.45(6)
C2	1.02897(17)	0.45464(17)	0.73001(12)	1.47(6)
C3	1.18609(18)	0.47509(19)	0.77092(13)	1.71(7)
C4	1.28828(19)	0.59665(19)	0.71567(13)	2.04(7)
C5	1.24003(20)	0.70027(20)	0.61963(14)	2.07(7)
C6	1.08661(19)	0.68487(19)	0.57668(13)	1.88(6)
C7	0.98335(18)	0.56221(17)	0.63266(12)	1.55(6)
N8	0.82731(15)	0.51992(14)	0.60653(10)	1.55(5)
C9	0.73063(22)	0.60632(22)	0.51694(15)	2.09(7)
C10	0.77537(18)	0.38893(17)	0.68455(12)	1.45(6)
C11	0.61236(18)	0.31016(18)	0.67917(13)	1.52(6)
C12	0.59723(17)	0.15900(17)	0.76979(12)	1.43(6)
C13	0.66811(17)	0.17500(18)	0.87755(12)	1.42(6)
C14	0.86133(17)	0.20713(17)	0.85946(12)	1.43(6)
C15	0.93319(19)	0.22176(19)	0.96568(12)	1.73(6)
C16	0.84644(20)	0.34656(20)	1.00644(14)	1.94(7)
C17	0.65616(19)	0.31652(21)	1.02314(13)	1.86(6)
C18	0.57863(19)	0.29935(19)	0.92023(13)	1.66(7)
C19	0.41154(18)	0.10760(17)	0.78372(12)	1.57(6)
O20	0.32050(13)	0.08882(13)	0.86410(9)	2.22(5)
O21	0.36117(12)	0.08697(13)	0.68997(9)	2.05(5)
C22	0.18537(20)	0.04301(23)	0.69048(16)	2.29(8)
C23	0.69535(17)	0.03326(18)	0.73374(12)	1.59(6)
O24	0.78018(14)	0.05045(13)	0.65110(9)	2.47(5)
O25	0.67282(13)	-0.10075(12)	0.80911(9)	2.16(5)
C26	0.7582 (3)	-0.22989(22)	0.78582(19)	3.00(9)
H3	1.2228 (18)	0.4059 (18)	0.8369 (13)	1.3 (3)
H4	1.3938 (22)	0.6099 (20)	0.7455 (14)	2.7 (4)
H5	1.3151 (20)	0.7855 (19)	0.5817 (13)	2.0 (3)
H6	1.0527 (21)	0.7539 (20)	0.5100 (14)	2.3 (4)
H9a	0.788 (3)	0.623 (3)	0.4477 (21)	6.7 (7)
H9b	0.633 (4)	0.550 (3)	0.5099 (24)	9.4 (9)
H9c	0.701 (3)	0.700 (3)	0.5289 (21)	7.5 (7)
H11a	0.6074 (19)	0.2860 (19)	0.6110 (14)	1.9 (3)
H11b	0.5168 (19)	0.3757 (18)	0.6848 (12)	1.6 (3)
H13	0.6475 (17)	0.0787 (18)	0.9321 (12)	1.0 (3)
H14	0.9169 (17)	0.1109 (17)	0.8459 (11)	1.0 (3)
H15a	0.9159 (19)	0.1225 (19)	1.0220 (13)	1.8 (3)
H15b	1.0589 (21)	0.2386 (18)	0.9554 (12)	2.1 (3)
H16a	0.8675 (19)	0.4471 (19)	0.9503 (13)	1.7 (3)
H16b	0.8973 (20)	0.3514 (18)	1.0768 (14)	2.1 (3)
H17a	0.6347 (19)	0.2210 (19)	1.0817 (13)	1.9 (3)
H17b	0.6001 (20)	0.3995 (20)	1.0490 (13)	2.2 (3)
H18a	0.5866 (20)	0.3975 (20)	0.8649 (13)	1.9 (3)
H18b	0.4572 (20)	0.2753 (18)	0.9353 (13)	2.0 (3)

Table S4. Continued

H22a	0.1727 (21)	0.0292 (21)	0.6176 (15)	3.0 (4)
H22b	0.1632 (21)	-0.0528 (22)	0.7486 (15)	2.8 (4)
H22c	0.1130 (22)	0.1229 (21)	0.6998 (14)	2.4 (4)
H26a	0.717 (3)	-0.245 (3)	0.7130 (20)	6.1 (6)
H26b	0.724 (3)	-0.318 (3)	0.8408 (19)	5.3 (6)
H26c	0.876 (3)	-0.212 (3)	0.7752 (17)	4.9 (5)

^a Biso is the Mean of the Principal Axes of the Thermal Ellipsoid.

Table S5. Bond lengths for **5**.

C(1)-C(2)	1.4501(20)	C(14)-C(15)	1.5405(21)
C(1)-C(10)	1.3677(20)	C(14)-H(14)	1.032(15)
C(1)-C(14)	1.5167(21)	C(15)-C(16)	1.5230(22)
C(2)-C(3)	1.4085(20)	C(15)-H(15a)	0.996(17)
C(2)-C(7)	1.4215(21)	C(15)-H(15b)	1.006(16)
C(3)-C(4)	1.3814(23)	C(16)-C(17)	1.5292(22)
C(3)-H(3)	0.964(16)	C(16)-H(16a)	1.007(17)
C(4)-C(5)	1.4001(25)	C(16)-H(16b)	1.018(17)
C(4)-H(4)	0.959(18)	C(17)-C(18)	1.5286(22)
C(5)-C(6)	1.3836(23)	C(17)-H(17a)	0.991(18)
C(5)-H(5)	0.982(17)	C(17)-H(17b)	0.999(18)
C(6)-C(7)	1.3953(22)	C(18)-H(18a)	0.978(18)
C(6)-H(6)	0.962(18)	C(18)-H(18b)	0.987(16)
C(7)-N(8)	1.3818(18)	C(19)-O(20)	1.2007(18)
N(8)-C(9)	1.4538(20)	C(19)-O(21)	1.3456(18)
N(8)-C(10)	1.3803(19)	O(21)-C(22)	1.4520(18)
C(9)-H(9a)	0.95(3)	C(22)-H(22a)	0.986(19)
C(9)-H(9b)	0.96(3)	C(22)-H(22b)	0.990(20)
C(9)-H(9c)	0.93(3)	C(22)-H(22c)	0.953(19)
C(10)-C(11)	1.4957(20)	C(23)-O(24)	1.1989(18)
C(11)-C(12)	1.5404(21)	C(23)-O(25)	1.3401(19)
C(11)-H(11a)	0.960(17)	O(25)-C(26)	1.4475(20)
C(11)-H(11b)	0.974(16)	C(26)-H(26a)	1.047(24)
C(12)-C(13)	1.5598(20)	C(26)-H(26b)	0.94(3)
C(12)-C(19)	1.5348(20)	C(26)-H(26c)	0.949(23)
C(12)-C(23)	1.5412(20)	H(9a)-H(9b)	1.49(4)
C(13)-C(14)	1.5556(20)	H(9a)-H(9c)	1.54(4)
C(13)-C(18)	1.5420(21)	H(11a)-H(11b)	1.557(23)
C(13)-H(13)	0.969(16)		

Table S6. Bond angles for **5**.

C(2)-C(1)-C(10)	105.97(13)	C(13)-C(14)-C(15)	109.44(12)
C(2)-C(1)-C(14)	132.44(12)	C(13)-C(14)-H(14)	107.3(8)
C(10)-C(1)-C(14)	121.58(13)	C(15)-C(14)-H(14)	105.0(8)
C(1)-C(2)-C(3)	135.71(14)	C(14)-C(15)-C(16)	112.12(12)
C(1)-C(2)-C(7)	106.73(12)	C(14)-C(15)-H(15a)	108.3(9)
C(3)-C(2)-C(7)	117.56(14)	C(14)-C(15)-H(15b)	109.9(9)
C(2)-C(3)-C(4)	119.34(15)	C(16)-C(15)-H(15a)	108.8(9)
C(2)-C(3)-H(3)	120.9(9)	C(16)-C(15)-H(15b)	111.6(9)
C(4)-C(3)-H(3)	119.7(9)	H(15a)-C(15)-H(15b)	106.0(13)
C(3)-C(4)-C(5)	121.72(14)	C(15)-C(16)-C(17)	110.38(13)
C(3)-C(4)-H(4)	118.1(10)	C(15)-C(16)-H(16a)	108.5(9)
C(5)-C(4)-H(4)	120.1(10)	C(15)-C(16)-H(16b)	109.3(9)
C(4)-C(5)-C(6)	120.92(15)	C(17)-C(16)-H(16a)	109.0(8)
C(4)-C(5)-H(5)	120.2(9)	C(17)-C(16)-H(16b)	111.0(9)
C(6)-C(5)-H(5)	118.9(9)	H(16a)-C(16)-H(16b)	108.7(12)
C(5)-C(6)-C(7)	117.32(15)	C(16)-C(17)-C(18)	111.95(13)
C(5)-C(6)-H(6)	121.9(10)	C(16)-C(17)-H(17a)	109.1(9)
C(7)-C(6)-H(6)	120.8(10)	C(16)-C(17)-H(17b)	109.8(9)
C(2)-C(7)-C(6)	123.14(14)	C(18)-C(17)-H(17a)	108.3(9)
C(2)-C(7)-N(8)	108.00(13)	C(18)-C(17)-H(17b)	111.2(9)
C(6)-C(7)-N(8)	128.84(14)	H(17a)-C(17)-H(17b)	106.2(13)
C(7)-N(8)-C(9)	125.25(13)	C(13)-C(18)-C(17)	111.58(12)
C(7)-N(8)-C(10)	108.11(12)	C(13)-C(18)-H(18a)	110.1(9)
C(9)-N(8)-C(10)	126.48(13)	C(13)-C(18)-H(18b)	110.4(9)
N(8)-C(9)-H(9a)	113.9(15)	C(17)-C(18)-H(18a)	108.7(9)
N(8)-C(9)-H(9b)	110.3(18)	C(17)-C(18)-H(18b)	109.4(9)
N(8)-C(9)-H(9c)	109.0(16)	H(18a)-C(18)-H(18b)	106.5(13)
H(9a)-C(9)-H(9b)	102.8(22)	C(12)-C(19)-O(20)	126.95(13)
H(9a)-C(9)-H(9c)	109.5(22)	C(12)-C(19)-O(21)	109.64(12)
H(9b)-C(9)-H(9c)	111.2(24)	O(20)-C(19)-O(21)	123.40(13)
C(1)-C(10)-N(8)	111.18(13)	C(19)-O(21)-C(22)	115.52(12)
C(1)-C(10)-C(11)	126.84(14)	O(21)-C(22)-H(22a)	104.3(10)
N(8)-C(10)-C(11)	121.97(13)	O(21)-C(22)-H(22b)	109.1(10)
C(10)-C(11)-C(12)	110.24(12)	O(21)-C(22)-H(22c)	110.5(10)
C(10)-C(11)-H(11a)	110.5(9)	H(22a)-C(22)-H(22b)	112.0(14)
C(10)-C(11)-H(11b)	110.8(9)	H(22a)-C(22)-H(22c)	109.2(14)
C(12)-C(11)-H(11a)	107.4(10)	H(22b)-C(22)-H(22c)	111.6(14)
C(12)-C(11)-H(11b)	110.5(9)	C(12)-C(23)-O(24)	125.95(14)
H(11a)-C(11)-H(11b)	107.2(13)	C(12)-C(23)-O(25)	109.91(12)
C(11)-C(12)-C(13)	111.53(12)	O(24)-C(23)-O(25)	124.14(14)
C(11)-C(12)-C(19)	108.18(12)	C(23)-O(25)-C(26)	115.94(14)
C(11)-C(12)-C(23)	109.73(12)	O(25)-C(26)-H(26a)	109.5(13)
C(13)-C(12)-C(19)	112.57(12)	O(25)-C(26)-H(26b)	107.8(14)
C(13)-C(12)-C(23)	108.94(11)	O(25)-C(26)-H(26c)	111.2(13)
C(19)-C(12)-C(23)	105.71(11)	H(26a)-C(26)-H(26b)	106.4(19)

Table S6. Continued

C(12)-C(13)-C(14)	108.93(11)	H(26a)-C(26)-H(26c)	106.2(18)
C(12)-C(13)-C(18)	113.01(12)	H(26b)-(26)-H(26c)	115.5(20)
C(12)-C(13)-H(13)	107.2(8)	C(9)-H(9a)-H(9b)	38.8(15)
C(14)-C(13)-C(18)	110.81(12)	C(9)-H(9a)-H(9c)	34.8(14)
C(14)-C(13)-H(13)	109.8(8)	H(9b)-H(9a)-H(9c)	61.9(18)
C(18)-C(13)-H(13)	107.0(8)	C(9)-H(9b)-H(9a)	38.4(15)
C(1)-C(14)-C(13)	108.67(11)	C(9)-H(9c)-H(9a)	35.6(14)
C(1)-C(14)-C(15)	114.95(12)	C(11)-H(11a)-H(11b)	36.7(8)
C(1)-C(14)-H(14)	111.2(8)	C(11)-H(11b)-H(11a)	36.1(8)

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