Supporting Information for
Cyclization Reactions of Homopropargyl Azide Derivatives
Catalyzed by PtCl₄ in Ethanol Solution: Synthesis of
Functionalized Pyrrole Derivatives

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Contents List for the Supporting Information

compound Name or Title	structure	page	¹ H-NMR	¹³ C-NMR
General Procedures		S4		
(1 <i>R</i> *,2 <i>S</i> *)-2-(Phenylethynyl)cyclohexanol (S-2)		S4	known compound	
2-[(1 <i>S</i> *,2 <i>S</i> *)-2-Phenylethynylcyclohexyl]-isoindole-1,3-dione (S-3)		S5	S29	S30
4-Methyl- <i>N</i> -[(1 <i>S</i> *,2 <i>S</i> *)-2-phenylethynylcyclohexyl]benzenesulfonamide (1)		S6	S31	S32
[(1 <i>S</i> *,2 <i>S</i> *)-2-Azidocyclohexylethynyl]benzene (3)		S7	S33	S34
(1 <i>R</i> *,2 <i>S</i> *)-2-(6- <i>tert</i> -Butyldiphenylsilyloxy-1-hexynyl)cyclohexanol (S-4)		S7	S35	S36
{6-[(1 <i>S</i> *,2 <i>S</i> *)-2-Azidocyclohexyl]hex-5-ynyloxy}- <i>tert</i> -butyldiphenylsilane (9)		S8	S37	S38
6-[(1 <i>S</i> *,2 <i>S</i> *)-2-Azidocyclohexyl]hex-5-yl-1-ol (5)		S9	S39	S40
(1 <i>R</i> *,2 <i>S</i> *)-2-(Pentylethynyl)cyclohexanol (S-5)		S9	S41	S42
(1 <i>S</i> *,2 <i>S</i> *)-1-Azido-2-(hept-1-ynyl)cyclohexane (7)		S10	S43	S44
(1 <i>S</i> *,2 <i>S</i> *)-6-(2-Azidocyclohexyl)hex-5-ynoic Acid Ethyl Ester (11)		S11	S45	S46
(1 <i>S</i> *,2 <i>S</i> *)- <i>N</i> -(<i>tert</i> -butoxycarbonyl)- <i>p</i> -toluenesulfonyl-6-(2-azidocyclohexyl)hex-2-ynylamide (13)		S12	S47	S48
(4-Azidobut-1-ynyl)benzene (15)		S13	S49	S50
Octadec-1-en-4-yne (S-8)		S13	known compound	

Octadec-4-yn-1,2-diol (S-9)		S14	known compound	
2-Azido-octadec-4-yn-1-ol (S-10)		S15	known compound	
2-Azido-octadec-4-ynoic acid Ethyl Ester (17)		S15	S51	S52
4-Azide-1,4-diphenyl-1-butyne (19)		S16	S53	S54
2-Phenyl-1-(toluene-4-sulfonyl)-3a,4,5,6,7,7a-hexahydroindole (2) (Scheme 1)		S17	S55	S56
2-Phenyl-4,5,6,7-tetrahydro-1H-indole (4) (Scheme 2)		S18	S57	S58
Experimental Procedures for Table 1		S19		
Experimental Procedures for Table 2 4-(4,5,6,7-Tetrahydro-1H-indol-2-yl)butan-1-ol (6)		S20	S59	S60
General Procedure for Table 3		S22		
2-Pentyl-4,5,6,7-tetrahydro-1H-indole (8) (Entry 3)		S22	S61	S62
2-[4-(tert-Butyldiphenylsilyloxy)butyl]-4,5,6,7-tetrahydro-1H-indole (10) (Entry 4)		S23	S63	S64
4-(4,5,6,7-Tetrahydro-1H-indol-2-yl)butyric Acid Ethyl Ester (12) (Entry 5)		S23	S65	S66
N-(tert-butoxycarbonyl)-p-toluenesulfonyl-6-(4,5,6,7-tetrahydro-1H-indol-2-yl)butylamide (14) (Entry 6)		S24	S67	S68
2-Phenyl-1H-pyrrole (16) (Entry 7)		S24	S69	S70
2-Tridecyl-1H-pyrrole-2-carboxylic Acid Ethyl Ester (18) (Entry 8)		S25	S71	S72
2,5-Diphenylpyrrole (20) (Entry 9)		S25	S73	S74
Experimental Procedure for Table 3 under Aerobic Condition		S26		
References		S28		

General Procedures

All melting points were determined with Yazawa Micro Melting Point BY-2 and are uncorrected. ^1H -NMR spectra (400 and 600 MHz) were recorded on JEOL JMN AL-400 and JEOL ECA-600 spectrometers, respectively. ^{13}C -NMR spectra (100 and 150 MHz) were recorded on JEOL JMN AL-400 and JEOL ECA-600 spectrometers, respectively. For ^1H -NMR spectra, chemical shifts (δ) are given from TMS (0 ppm) in CDCl_3 and from residual non-deuterated solvent peak in the other solvents (methanol- d_4 : 3.30 ppm, benzene- d_6 : 7.15 ppm) as internal standards. For ^{13}C -NMR spectra, chemical shifts (δ) are given from $^{13}\text{CDCl}_3$ (77.0 ppm) and $^{13}\text{CD}_3\text{OD}$ (49.0 ppm) as internal standards. Mass spectra, high resolution mass spectra, and fast atom bombardment mass spectra were measured on JEOL JMS-DX303, MS-AX500, and JMS-DX700 instruments, respectively. IR spectra were recorded on a Shimadzu FTIR-8400. Elemental analysis was measured on Yanaco CHN CORDER MT-6.

Synthesis of the Substrates

Synthesis of 1

(1*R,2*S**)-2-(Phenylethynyl)cyclohexanol (S-2).**^{S1} Butyllithium (1.26 M solution in hexane, 6.0 ml, 7.5 mmol) was slowly added to a solution of ethynylbenzene (0.818 ml, 7.5 mmol) in THF (50 ml) at $-78\text{ }^\circ\text{C}$. After being stirred for 30 min, 1,2-epoxycyclohexane (**S-1**) (0.51 ml, 5.0 mmol) and boron trifluoride diethyl ether complex (0.950 ml, 7.5 mmol) were successively added to a reaction mixture at $-78\text{ }^\circ\text{C}$ and the reaction mixture was stirred for 4 h at $-78\text{ }^\circ\text{C}$. Saturated aqueous NH_4Cl solution was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO_4 , and

concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:4)] to afford **S-2** (1.03 g, 100%) as a yellow oil; IR (neat, cm^{-1}) 3381, 2230, 1599, 1491, 1445; ^1H -NMR (400 MHz, CDCl_3) δ 1.18-1.40 (3H, m), 1.44-1.53 (1H, m), 1.66-1.75 (1H, m), 1.75-1.83 (1H, m), 2.02-2.11 (2H, m), 2.36 (1H, br s), 2.43 (1H, ddd, $J = 11.6, 9.2, 3.6$ Hz), 3.55 (1H, td, $J = 9.5, 3.6$ Hz), 7.26-7.32 (3H, m), 7.38-7.44 (2H, m); ^{13}C -NMR (100 MHz, CDCl_3) δ 24.3, 24.9, 31.1, 33.2, 39.6, 73.6, 82.7, 90.8, 123.2, 127.8, 128.1, 131.6; MS m/z 200 (M^+ , 22.0), 57 (100), 171 (5.2), 80 (41.2); HRMS Calcd $\text{C}_{14}\text{H}_{16}\text{O}$: 200.1201. Found: 200.1190.

2-[(1*S,2*S**)-2-Phenylethynylcyclohexyl]isoindole-1,3-dione (**S-3**). **S-2** (198 mg, 0.99 mmol) and diethyl azodicarboxylate (40% solution in toluene, 1.3 ml, 3.0 mmol) was slowly added to the solution of triphenylphosphine (1.12 g, 4.5 mmol) and phthalimide (437 mg, 2.97 mmol) in THF (25 ml) at 0 °C. After being stirred at room temperature for 6 h, the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:5)] to afford **S-3** (196 mg, 60%) as a colorless solid; mp 152-153 °C (colorless plate from ethyl acetate-hexane); IR (film, cm^{-1}) 2936, 2858, 1771, 1709, 1489, 1394, 1367, 1328; ^1H -NMR (400 MHz, CDCl_3) δ 1.21-1.51 (1H, m), 1.60-2.12 (6H, m), 3.21 (1H, qd, $J = 13.8, 2.6$ Hz), 3.33 (1H, m), 4.21 (1H, dt, $J = 13.8, 3.7$ Hz), 7.24-7.26 (3H, m), 7.40-7.42 (2H, m), 7.67 (2H, dd, $J = 5.1, 2.9$ Hz), 7.81 (2H, dd, $J = 5.1, 2.9$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 21.2, 25.3, 26.4, 31.1, 33.9, 55.2, 83.6, 89.4, 122.9, 123.7, 127.5, 128.0, 131.5, 131.8, 133.6, 168.5; MS m/z 329 (M^+ , 36.7), 182 (100); HRMS Calcd $\text{C}_{22}\text{H}_{19}\text{NO}_2$: 329.1416. Found: 329.1430; *Anal.* Calcd $\text{C}_{22}\text{H}_{19}\text{NO}_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.29; H, 6.00; N, 4.25.**

4-Methyl-N-[(1*S,2*S**)-2-phenylethynylcyclohexyl]benzenesulfonamide (1).** Hydrazine

monohydrate (31.6 μ l, 0.619 mmol) was added to a solution of **S-3** (185 mg, 0.56 mmol) in ethanol (10 ml) and the mixture was refluxed for 2 h. After being cooled, concentrated HCl was added to the reaction mixture and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure and H₂O was added to the residue. The precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was used to the next reaction without further purification.

Triethylamine (0.64 ml, 4.56 mmol) and *p*-toluenesulfonyl chloride (218 mg, 2.18 mmol) were added to a solution of amine hydrochloride salt in chloroform (10 ml) at 0 °C and stirred at room temperature for 1 day. Saturated aqueous NH₄Cl solution was added to the mixture and the aqueous phase was extracted with chloroform. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:5)] to afford **1** (172 mg, 54%) as a colorless solid; mp 144-145 °C (colorless plate from ethyl acetate-hexane); IR (film, cm⁻¹) 3279, 2936, 2858, 1597, 1325, 1161; ¹H-NMR (400 MHz, CDCl₃) δ 1.12-1.31 (1H, m), 1.47-1.71 (6H, m), 1.84-1.90 (1H, m), 2.41 (3H, s), 2.90 (1H, d, *J* = 4.0 Hz), 3.24-3.37 (1H, m), 4.89 (1H, d, *J* = 9.2 Hz), 7.26 (2H, d, *J* = 8.0 Hz), 7.27-7.30 (3H, m), 7.37-7.38 (2H, m), 7.77 (2H, d, *J* = 8.0 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 21.0, 21.5, 24.7, 30.0, 30.3, 34.7, 53.9, 84.9, 88.0, 122.9, 126.8, 128.0, 128.2, 129.5, 131.6, 138.5, 143.1; MS *m/z* 353 (M⁺, 12.2), 289 (25.6), 198 (100), 182 (88.3), 91 (50.2); HRMS Calcd C₂₁H₂₃NO₂S: 353.1450. Found: 353.1441; *Anal.* Calcd C₂₁H₂₃NO₂S: C, 71.36; H, 6.56; N, 3.96. Found: C, 71.46; H, 6.56; N, 3.99.

Synthesis of 3

[(1*S,2*S**)-2-Azidocyclohexylethynyl]benzene (3).** Diethyl azodicarboxylate (40% solution in toluene, 1.9 ml, 4.5 mmol) was slowly added to a solution of triphenylphosphine (1.12 g, 4.5 mmol) in THF (25 ml) at 0 °C. After being stirred for 30 min, the mixture was added to a solution of **S-2** (596 mg, 3.0 mmol) in THF (10 ml) at 0 °C and stirring was continued at the same temperature. After 30 min, diphenylphosphoryl azide (47 μ l, 0.22 mmol) was added to the mixture and stirred at room temperature for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:50)] to afford **3** (500 mg, 74%) as a slightly yellow oil; IR (neat, cm^{-1}) 2095, 1597, 1488, 1443, 1263; ^1H -NMR (400 MHz, CDCl_3) δ 1.36-1.50 (2H, m), 1.58-1.85 (4H, m), 1.88-2.00 (2H, m), 3.05-3.10 (1H, m), 3.45-3.52 (1H, m), 7.25-7.32 (3H, m), 7.40-7.46 (2H, m); ^{13}C -NMR (100 MHz, CDCl_3) δ 22.1, 23.2, 27.9, 29.7, 34.6, 61.1, 83.9, 89.0, 123.4, 127.7, 128.1, 131.6; MS m/z 225 (M^+ , 49.3), 154 (100), 196 (44.2), 182 (19.7), 169 (33.8); HRMS Calcd $\text{C}_{14}\text{H}_{15}\text{N}_3$: 225.1266. Found: 225.1252.

Synthesis of 5 and 9

(1*R,2*S**)-2-(6-*tert*-Butyldiphenylsilyloxy-1-hexynyl)cyclohexanol (S-4).** Butyllithium (1.40 M solution in hexane, 0.76 ml, 1.1 mmol) was added to a solution of 1-*tert*-butyldiphenylsilyloxy-5-hexyne^{S2} (297 mg, 0.9 mmol) in THF (9.0 ml) at -78°C , and stirred for 30 min. 1,2-Epoxycyclohexane (**S-1**) (0.089 ml, 1.1 mmol) and boron trifluoride diethyl ether complex (0.130 ml, 1.1 mmol) were successively added to the reaction mixture at -78°C and the reaction mixture

was stirred for 4 h at the same temperature. The reaction mixture was warmed to room temperature. Saturated aqueous NH_4Cl solution was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO_4 , and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:5)] to afford **S-4** (326.3 mg, 85%) as a pale yellow oil; IR (neat, cm^{-1}) 3385, 1427, 1111; ^1H -NMR (400 MHz, CDCl_3) δ 1.05 (9H, s), 1.10-1.44 (5H, m), 1.59-1.73 (6H, m), 1.86-2.05 (2H, m), 2.18-2.25 (3H, m), 3.36 (1H, td, $J = 9.6, 4.0$ Hz), 3.67 (2H, t, $J = 6.0$ Hz), 7.35-7.41 (6H, m), 7.66 (4H, dd, $J = 8.0, 1.6$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 18.5, 19.2, 24.3, 24.9, 25.5, 26.9, 31.4, 31.7, 33.0, 39.1, 63.4, 73.7, 81.3, 82.5, 127.5, 129.4, 133.8, 135.4; MS m/z 377 ($\text{M}^+ - \text{tert-Bu}$, $\text{C}_{24}\text{H}_{29}\text{O}_2\text{Si}^+$, 12.0), 199 (100), 359 (2.3), 279 (18.2); HRMS Calcd $\text{C}_{24}\text{H}_{29}\text{O}_2\text{Si}$: 377.1937. Found: 377.1923.

{6-[(1*S,2*S**)-2-Azidocyclohexyl]hex-5-ynyloxy}-*tert*-butyldiphenylsilane (9).** Diethyl azodicarboxylate (40% solution in toluene, 0.19 ml, 0.45 mmol) was slowly added to a solution of triphenylphosphine (117.4 mg, 0.45 mmol) in THF (2.0 ml) at 0 °C. After being stirred for 30 min, the mixture and diphenylphosphoryl azide (0.46 ml, 2.1 mmol) was successively added to a solution of **S-4** (129.7 mg, 0.3 mmol) in THF (1 ml) at 0 °C and stirred at room temperature for 2 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:100)] to afford **9** (83.4 mg, 61%) as a colorless oil; IR (film, cm^{-1}) 2095, 1427, 1111; ^1H -NMR (400 MHz, CDCl_3) δ 1.05 (9H, s), 1.25-1.42 (2H, m), 1.45-1.53 (1H, m), 1.58-1.90 (9H, m), 2.21 (2H, td, $J = 6.4, 2.0$ Hz), 2.78-2.85 (1H, m), 3.35-3.40 (1H, m), 3.68 (2H, t, $J = 6.4$ Hz), 7.34-7.41 (6H, m), 7.64-7.67 (4H, m); ^{13}C -NMR (100MHz, CDCl_3) δ 18.7, 19.3, 22.0, 23.3, 25.4, 26.9, 27.8, 30.0, 31.8, 33.9, 61.3, 63.5, 79.3, 83.9, 127.5, 129.4, 134.0, 135.5; MS m/z 402 ($\text{M}^+ - \text{tert-Bu}$,
S8

$C_{24}H_{28}N_3OSi^+$, 25.4), 374 (100), 280 (64.8), 199 (75.9); HRMS Calcd $C_{24}H_{28}N_3OSi$: 402.2002. Found: 402.1997.

6-[(1*S,2*S**)-2-Azidocyclohexyl]hex-5-yl-1-ol (5).** TBAF (1.0 M solution in THF, 77 μ l, 77 μ mol) was added to a solution of **9** (17.7 mg, 38.5 μ mol) in THF (0.5 ml) and stirred at room temperature for 1 h. H_2O was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:3)] to afford **5** (7.6 mg, 89%) as a colorless oil; IR (film, cm^{-1}) 3333, 2095, 1447, 1259, 1061; 1H -NMR (400 MHz, $CDCl_3$) δ 1.25-1.43 (2H, m), 1.47-1.90 (11H, m), 2.25 (2H, td, $J = 6.6, 2.3$ Hz), 2.80-2.88 (1H, m), 3.38-3.44 (1H, m), 3.67 (2H, t, $J = 6.6$ Hz); ^{13}C -NMR (100 MHz, $CDCl_3$) δ 18.6, 22.0, 23.2, 25.1, 27.8, 29.8, 31.9, 33.8, 61.3, 62.4, 79.5, 83.6; MS m/z 192 ($M^+ - HN_2$, $C_{12}H_{18}NO^+$, 9.7), 91 (100), 150 (40.9), 134 (58.6); HRMS Calcd $C_{12}H_{18}NO$: 192.1388. Found: 192.1364.

Synthesis of 7

(1*R,2*S**)-2-(Pentylethynyl)cyclohexanol (S-5).** Butyllithium (1.26 M solution in hexane, 6.0 ml, 7.5 mmol) was slowly added to a solution of 1-heptyne (0.27 ml, 2.4 mmol) in THF (20 ml) at $-78^\circ C$. After being stirred for 30 min, 1,2-epoxycyclohexane (**S1**) (0.2 ml, 2.0 mmol) and boron trifluoride diethyl ether complex (0.3 ml, 2.4 mmol) were successively added to the reaction mixture at $-78^\circ C$ and stirred

for 4 h at the same temperature. The reaction mixture was warmed to room temperature and saturated aqueous NH_4Cl solution was added to the mixture. The aqueous phase was extracted with ethyl acetate and the combined organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO_4 , and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:10)] to afford **S-5** (260 mg, 68%) as a pale yellow oil; IR (film, cm^{-1}) 3412, 1448, 1067; ^1H -NMR (400 MHz, CDCl_3) δ 0.90 (3H, t, $J = 7.2$ Hz), 1.10-1.40 (8H, m), 1.45-1.53 (2H, m), 1.60-1.72 (1H, m), 1.70-1.77 (1H, m), 1.90-2.02 (2H, m), 2.10-2.20 (3H, m), 2.34 (1H, br s), 3.37 (1H, td, $J = 7.2, 2.1$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 14.0, 18.8, 22.2, 24.4, 25.0, 28.8, 31.1, 31.4, 33.0, 39.2, 73.9, 81.0, 82.8; MS m/z 194 (M^+ , 10.9), 82 (100), 165 (11.1), 138 (66.5); HRMS Calcd $\text{C}_{13}\text{H}_{22}\text{O}$: 194.1671. Found: 194.1653.

(1S*,2S*)-1-Azido-2-(hept-1-ynyl)cyclohexane (7). Diethyl azodicarboxylate (40% solution in toluene, 0.86 ml, 2.0 mmol) was slowly added to a solution of triphenylphosphine (520 mg, 2.0 mmol) in THF (8 ml) at 0 °C. After being stirred for 20 min, the mixture and diphenylphosphoryl azide (0.46 ml, 2.1 mmol) were successively added to a solution of **S-5** (258.7 mg, 1.4 mmol) in THF (5 ml) at 0 °C and stirred at room temperature for 2 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:100)] afford to **7** (156 mg, 54%) as a colorless oil; IR (film, cm^{-1}) 2095, 1447, 1259; ^1H -NMR (400 MHz, CDCl_3) δ 0.90 (3H, t, $J = 7.1$ Hz), 1.28-1.42 (6H, m), 1.45-1.55 (3H, m), 1.60-1.90 (5H, m), 2.19 (2H, td, $J = 7.1, 2.1$ Hz), 2.80-2.86 (1H, m), 3.36-3.42 (1H, m); ^{13}C -NMR (100 MHz, CDCl_3) δ 14.1, 18.8, 22.0, 22.2, 23.3, 27.8, 28.6, 30.0, 31.1, 33.9, 61.3, 79.1, 84.1; MS m/z 219 (M^+ , 0.4), 190 ($\text{M}^+ - \text{HN}_2$, $\text{C}_{13}\text{H}_{20}\text{N}^+$, 11.7), 134 (100); HRMS Calcd $\text{C}_{13}\text{H}_{20}\text{N}$: 190.1596. Found: 190.1579.

Synthesis of 11

(1S*,2S*)-6-(2-Azidocyclohexyl)hex-5-ynoic Acid Ethyl Ester (11). Dess-Martin periodinate (DMP) (93.3 mg, 0.22 mmol) was added to a solution of **5** (44.3 mg, 0.20 mmol) in dichloromethane (2.0 ml) at room temperature and stirred at same temperature for 10 min. Saturated aqueous Na₂S₂O₃ solution and saturated aqueous NaHCO₃ solution were successively added to the reaction mixture and the aqueous phase was extracted with ethyl acetate. The combined organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and the solvent was evaporated to provide the aldehyde, which was used to the next reaction without further purification.

2-Methyl-2-butene (2.0 M solution in THF, 0.2 ml, 0.40 mmol), NaClO₂ (27.1 mg, 0.30 mmol), and NaH₂PO₄·2H₂O (46.8 mg, 0.30 mmol) were successively added to a solution of the aldehyde in *tert*-butanol (2.0 ml) and H₂O (0.5 ml). After being stirred at room temperature for 30 min, saturated aqueous NH₄Cl solution was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated to afford the crude carboxylic acid, which was used to the next reaction without further purification.

SOCl₂ (16.1 µl, 0.22 mmol) was added to a solution of the crude carboxylic acid in ethanol (2.0 ml) at 0 °C. After being stirred at room temperature for 30 min, the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:15)] to afford **11** (36.8 mg, 70%) as a colorless oil; IR (film, cm⁻¹) 2095, 1734, 1448, 1373, 1258, 1159; ¹H-NMR (400 MHz CDCl₃) δ 1.26 (3H, t, *J* = 7.1 Hz), 1.28-1.43 (2H, m), 1.47-1.56 (1H, m), 1.57-1.90

(7H, m), 2.28 (2H, td, $J = 7.2, 2.0$ Hz), 2.44 (2H, t, $J = 7.2$ Hz), 2.80-2.85 (1H, m), 3.36-3.44 (1H, m), 4.13 (2H, q, $J = 7.1$ Hz); ^{13}C -NMR (100 MHz CDCl_3) δ 14.3, 18.3, 22.0, 23.3, 24.1, 27.8, 29.8, 33.2, 33.8, 60.3, 61.2, 80.1, 82.7, 173.1; MS m/z 263 (M^+ , 11.2), 134 (100), 235 (7.9), 221 (10.5), 206 (25.8), 190 (23.7), 148 (98.2); HRMS Calcd $\text{C}_{14}\text{H}_{21}\text{N}_3\text{O}_2$: 263.1634. Found: 192.1364.

Synthesis of 13

(1*S**,2*S**)-*N*-(*tert*-butoxycarbonyl)-*p*-toluenesulfonyl-6-(2-azidocyclohexyl)hex-2-ynylamide (**13**).

Diethyl azodicarboxylate (40% solution in toluene, 23 μl , 51.5 μmol) was slowly added to a solution of triphenylphosphine (13.5 mg, 51.5 μmol) in benzene (0.25 ml) at 0 °C. After being stirred for 10 min, **5** (7.6 mg, 34.3 μmol) in benzene (0.15 ml) and *N*-(*tert*-butoxy-carbonyl)-*p*-toluenesulfonamide (14.0 mg, 51.5 μmol) were successively added to the mixture at 0 °C and stirred at room temperature for 50 min. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:9)] to afford **13** (7.6 mg, 47%) as a colorless oil; IR (film, cm^{-1}) 2936, 2095, 1728, 1357, 1258, 1157, 719, 675; ^1H -NMR (400 MHz, CDCl_3) δ 1.35 (9H, s), 1.58-1.92 (14H, m), 2.44 (3H, s), 2.84 (1H, m), 3.39 (1H, d, $J = 9.6$ Hz), 3.84 (2H, t, $J = 7.2$ Hz), 7.29 (2H, d, $J = 8.0$ Hz), 7.77 (2H, d, $J = 8.0$ Hz); ^{13}C -NMR (150 MHz, CDCl_3) δ 18.5, 21.6, 21.9, 23.2, 26.0, 27.7, 27.8, 29.5, 29.8, 33.8, 46.7, 61.2, 79.7, 83.4, 84.0, 127.8, 129.2, 137.5, 144.0, 150.9; MS m/z 446 ($\text{M}^+ - \text{N}_2$, 10.7), 174 (70.8), 191 (72.4), 155 (77.7), 91 (100), 57 (94.2); HRMS Calcd $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_4\text{S}$: 446.2239. Found: 446.2255.

Synthesis of 15

(4-Azidobut-1-ynyl)benzene (15). Sodium azide (144 mg, 2.22 mmol) was added to a solution of toluene-4-sulfonic acid 4-phenyl-but-3-ynyl ester (**S-6**)^{S3} (606 mg, 2.02 mmol) in DMF (20 ml) and stirred at 0 °C to room temperature for 23 h. H₂O was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:15)] to afford **15** (339 mg, 98%) as a colorless oil; IR (film, cm⁻¹) 2106, 1489, 1443, 1263, 756, 691; ¹H-NMR (400 MHz, CDCl₃) δ 2.71 (2H, t, *J* = 6.8 Hz), 3.47 (2H, t, *J* = 6.8 Hz), 7.25-7.42 (5H, m); ¹³C-NMR (100 MHz, CDCl₃) δ 20.7, 50.0, 82.5, 85.7, 123.1, 128.0, 128.2, 131.5; MS *m/z* 171 (M⁺, 20.7), 115 (100); HRMS Calcd C₁₀H₉N₃: 171.0796. Found: 171.0780.

Synthesis of 17

Octadec-1-en-4-yne (S-8).^{S4} Butyllithium (1.57 M solution in hexane, 8.2 ml, 12.9 mmol) was added to the solution of 1-pentadecyne (**S-7**) (1.34 g, 6.43 mmol) in THF (65 ml) at −78 °C over 30 min and stirred for 30 min at −20 °C. Allyl bromide (1.64 ml, 19.3 mmol) was added to the reaction mixture and stirred for 2.5 days. Saturated aqueous NH₄Cl solution was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated. The residue was purified by silica gel column

chromatography (hexane) to afford **S-8** (862 mg, 55%) as a colorless oil; IR (film, cm^{-1}) 2924, 2853, 2359, 2341, 1641, 1466, 1420, 989, 914, 800; ^1H -NMR (400 MHz, CDCl_3) δ 0.88 (3H, t, $J = 6.8$ Hz), 1.26-1.54 (22H, m), 2.18 (2H, tt, $J = 8.0, 2.4$ Hz), 2.94 (2H, m), 5.09 (1H, dq, $J = 10.0, 1.8$ Hz), 5.31 (1H, dq, $J = 16.0, 1.8$ Hz), 5.82 (1H, ddt, $J = 16.0, 10.0, 5.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 14.2, 18.9, 22.8, 23.2, 29.0, 29.1, 29.2, 29.4, 29.6, 29.70, 29.71, 29.73, 29.8, 32.0, 76.4, 83.0, 115.5, 133.3; MS m/z : 248 (M^+ , 1.8), 79 (100); HRMS Calcd $\text{C}_{18}\text{H}_{32}$: 248.2504. Found: 248.2527.

Octadec-4-yn-1,2-diol (S-9).^{S4} OsO_4 (0.05 M solution in THF, 2.0 ml, 0.1 mmol) was added to a solution of 4-methylmorpholine *N*-oxide (NMO) (834 mg, 7.12 mmol) in H_2O (10 ml) and ethyl acetate (10 ml). **S-8** (862 mg, 3.47 mmol) in acetone (10 ml) was added to the mixture and stirred for 1 h at room temperature. Saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution was added to the reaction mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO_4 , and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:2)] to afford **S-9** (630 mg, 87%) as a colorless solid; mp 92-94 $^\circ\text{C}$ (colorless plate from ethyl acetate-hexane); IR (film, cm^{-1}) 3242, 2918, 2849, 1464, 1076; ^1H -NMR (400 MHz, CDCl_3) δ 0.88 (3H, t, $J = 6.8$ Hz), 1.26-1.37 (21H, m), 1.45-1.52 (1H, m), 1.90 (1H, m), 2.15 (2H, tt, $J = 6.0, 2.4$ Hz), 2.29 (1H, d, $J = 4.4$ Hz), 2.41 (2H, dt, $J = 6.0, 2.4$ Hz), 3.57-3.61 (1H, m), 3.72-3.75 (1H, m), 3.82-3.84 (1H, m); ^{13}C -NMR (100 MHz, CDCl_3) δ 0.1, 6.2, 14.2, 18.8, 22.8, 24.0, 29.0, 29.2, 29.4, 29.6, 29.72, 29.75, 32.0, 65.7, 70.3, 76.7, 83.7, 93.5; MS m/z 282 (M^+ , 3.2), 251 (39.1), 95 (100); HRMS Calcd $\text{C}_{18}\text{H}_{34}\text{O}_2$: 282.2559. Found: 282.2547.

2-Azido-octadec-4-yn-1-ol (S-10).^{S5} Diethyl azodicarboxylate (40% solution in toluene, 0.92 ml, 2.1 mmol) was slowly added to a solution of triphenylphosphine (553 mg, 2.11 mmol) in dichloromethane (5.0 ml) at 0 °C. After being stirred for 30 min, the mixture was added to a solution of **S-9** (129.7 mg, 0.3 mmol) in dichloromethane (5 ml) at 0 °C and the stirring was continued for 2 h at the same temperature. TMSN₃ (0.21 ml, 1.58 mmol) was added to the reaction mixture and stirred at room temperature for 12 h. TBAF (1.0 M solution in THF, 2.1 ml, 2.1 mmol) was added to the reaction mixture and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:8 to 1:5)] to afford **S-10** (179 mg, 55%) as a colorless oil; IR (film, cm⁻¹) 2924, 2855, 2110, 1466, 1444, 1344, 1263, 1051, 721; ¹H-NMR (600 MHz, CDCl₃) δ 0.88 (3H, t, *J* = 7.2 Hz), 1.26 (18H, m), 1.33-1.40 (2H, m), 1.48 (2H, quint, *J* = 7.2 Hz), 1.91 (1H, br s), 2.15 (2H, tt, *J* = 6.0, 2.3 Hz), 2.47 (2H, dt, *J* = 8.0, 2.9 Hz), 3.62-3.67 (2H, m), 3.78-3.80 (1H, m); ¹³C-NMR (150 MHz, CDCl₃) δ 14.1, 18.7, 21.4, 22.7, 28.7, 28.9, 29.1, 29.3, 29.5, 29.61, 29.64 (two peaks), 29.7, 31.9, 62.5, 64.2, 74.6, 83.7; MS *m/z* 307 (M⁺, 0.5), 95 (100); HRMS Calcd C₁₈H₃₃N₃O: 278.2484. Found: 278.2469.

2-Azido-octadec-4-ynoic acid Ethyl Ester (17). DMP (171 mg, 0.4 mmol) was added to a solution of **S-10** (82.4 mg, 0.26 mmol) in dichloromethane (2.7 ml) at room temperature and stirred for 4 h at the same temperature. Saturated aqueous Na₂S₂O₃ solution and saturated aqueous NaHCO₃ solution were successively added to the reaction mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous

MgSO₄, and the solvent was evaporated to provide the aldehyde, which was used to the next reaction without further purification.

2-Methyl-2-butene (2.0 M solution in THF, 0.20 ml, 0.40 mmol), NaClO₂ (35.7 mg, 0.39 mmol), and NaH₂PO₄·2H₂O (61.6 mg, 0.39 mmol) were successively added to a solution of the aldehyde in *tert*-butanol (2.0 ml) and H₂O (0.5 ml). After being stirred at room temperature for 11 h, saturated aqueous NH₄Cl solution was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated to afford the crude carboxylic acid, which was used to the next reaction without further purification.

SOCl₂ (16.1 µl, 0.22 mmol) was added to a solution of the crude carboxylic acid in ethanol (2.0 ml) at 0 °C and stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:15)] to afford **17** (49.6 mg, 54%) as a colorless oil; IR (film, cm⁻¹) 2926, 2855, 2110, 1747, 1466, 1269, 1188, 669; ¹H-NMR (600 MHz, CDCl₃) δ 0.88 (3H, t, *J* = 7.2 Hz), 1.26 (18H, m), 1.32 (3H, t, *J* = 7.2 Hz), 1.35 (2H, m), 1.47 (2H, quint, *J* = 7.2 Hz), 2.14 (2H, tdd, *J* = 7.2, 2.6, 2.4), 2.67 (1H, ddt, *J* = 17.7, 7.4, 2.4), 2.73 (1H, ddt, *J* = 16.2, 5.4, 2.6), 3.93 (1H, dd, *J* = 7.4, 5.4 Hz), 4.25-4.30 (2H, m); ¹³C-NMR (150 MHz, CDCl₃) δ 14.1, 14.2, 18.7, 22.75, 22.78, 28.6, 28.8, 29.1, 29.3, 29.5, 29.59, 29.69, 29.71, 29.73, 31.9, 60.9, 62.0, 73.7, 84.2, 169.1; MS *m/z* 321 (M⁺-N₂, 5.7), 307 (46.2), 248 (60.4), 95 (100); HRMS Calcd C₂₀H₃₅NO₂: 321.2668. Found: 321.2650.

Synthesis of 19

4-Azide-1,4-diphenyl-1-butyne (19). Triethylamine (63.7 µl, 0.456 mmol) and methanesulfonyl chloride (13.3 µl, 0.171 mmol) were successively added to a solution of **S-11**^{S6} (25.4 mg, 0.114 mmol) in

dichloromethane (1.1 ml) and stirred at room temperature for 45 min. H₂O was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated to afford the crude mesylate, which was used to the next reaction without further purification.

Sodium azide (17.8 mg, 0.27 mmol) was added to a solution of the crude mesylate in DMF (1.1 ml) and stirred at room temperature for 17.5 h. H₂O was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and the solvent was evaporated under reduced pressure to afford **19** (25.3 mg, 90%) as a colorless oil; IR (film, cm⁻¹) 3032, 2926, 2853, 2098, 1598, 1491, 1454, 1248, 756, 692; ¹H-NMR (400 MHz, CDCl₃) δ 2.85 (1H, dd, *J* = 17.0, 6.3 Hz), 2.92 (1H, dd, *J* = 17.0, 7.5 Hz), 4.75 (1H, dd, *J* = 7.5, 6.3 Hz) 7.23-7.43 (10H, m); ¹³C-NMR (100 MHz, CDCl₃) δ 28.1, 63.7, 83.2, 85.4, 123.1, 126.8, 128.0, 128.2, 128.6, 128.8, 131.6, 138.5; MS *m/z* 247 (M⁺, 2.2), 204 (24.5), 132 (78.1), 116 (22.4), 115 (100), 77 (55.7); HRMS Calcd C₁₆H₁₃N₃: 247.1109. Found: 247.1114.

Platinum-catalyzed Cyclization Reactions

2-Phenyl-1-(toluene-4-sulfonyl)-3a,4,5,6,7,7a-hexahydroindole (2) (Scheme 1). PtCl₄ (171 mg, 0.4 mmol) was added to a solution of **1** (50 mg, 0.14 mmol) in dichloromethane (2.0 ml) at room temperature and the mixture was refluxed for 6.5 h. Saturated aqueous NH₄Cl solution was added to the mixture and the aqueous phase was extracted with chloroform. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:7)] to afford **2** (34 mg, 68%) as a

colorless solid; mp 143-144 °C (colorless plates from ethyl acetate-hexane); IR (film, cm^{-1}) 1597, 1352, 1167, 740, 665; ^1H -NMR (400 MHz, CDCl_3) δ 1.10-1.20 (2H, m), 1.33-1.39 (1H, m), 1.40-1.47 (1H, m), 1.57-1.68 (3H, m), 2.06-2.11 (1H, m), 2.37 (1H, t, $J = 4.5$ Hz), 2.43 (3H, s), 4.25 (1H, dt, $J = 7.2, 4.5$ Hz), 5.37 (1H, d, $J = 1.0$ Hz), 7.26 (2H, d, $J = 5.4$ Hz), 7.34-7.38 (3H, m), 7.57 (2H, dd, $J = 5.2, 1.0$ Hz), 7.61 (2H, d, $J = 5.4$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 21.3, 21.6, 22.3, 26.1, 28.8, 40.1, 63.7, 123.5, 127.1, 127.3, 127.8, 128.5, 129.3, 133.5, 135.8, 143.29, 143.33; MS m/z 353 (M^+ , 33.4), 198 (100), 197 (91.0) HRMS Calcd $\text{C}_{21}\text{H}_{23}\text{NO}_2\text{S}$: 353.1450. Found: 353.1457.

2-Phenyl-4,5,6,7-tetrahydro-1H-indole (4)^{S7} (Scheme 2). PtCl_4 (2.7 mg, 8.0 μmol) was added to a solution of **3** (35.3 mg, 0.16 mmol) in 1,2-dichloroethane (1.6 ml) at room temperature and stirred at 50 °C for 16 h. Saturated aqueous NaHCO_3 solution was added to the mixture and the aqueous phase was extracted with chloroform. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO_4 , and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:50)] to afford **4** (19.6 mg, 70%) as a colorless solid; mp 111-113 °C (colorless plates from ethyl acetate-hexane), lit.^{S7} 109-110 °C; IR (film, cm^{-1}) 3429, 754, 691; ^1H -NMR (400 MHz, CDCl_3) δ 1.73-1.90 (4H, m), 2.54 (2H, t, $J = 6.2$ Hz), 2.64 (2H, t, $J = 6.2$ Hz), 6.27 (1H, d, $J = 2.8$ Hz), 7.14 (1H, t, $J = 7.4$ Hz), 7.32 (2H, t, $J = 7.4$ Hz), 7.41 (2H, d, $J = 7.4$ Hz), 7.93 (1H, br s); ^{13}C -NMR (100 MHz, CDCl_3) δ 22.93, 22.95, 23.4, 23.8, 105.1, 118.9, 123.3, 125.4, 128.4, 128.7, 130.2, 133.1; MS m/z 197 (M^+ , 98.4), 169 (100), 196 (40.6); HRMS Calcd $\text{C}_{14}\text{H}_{15}\text{N}$: 197.1204. Found: 197.1178.

Experimental Procedures for Table 1.

Entry 1. PtCl₄ (2.7 mg, 8.0 μmol) was added to a solution of **3** (35.5 mg, 0.16 mmol) in 1,2-dichloroethane (1.6 ml) at room temperature and stirred at 50 °C for 16 h. Saturated aqueous NaHCO₃ solution was added to the mixture and the aqueous phase was extracted with chloroform. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:50)] to afford **4** (19.6 mg, 70%) as a colorless solid.

Entry 2. PtCl₄ (2.7 mg, 8.0 μmol) was added to a solution of **3** (39.3 mg, 0.17 mmol) in ethanol (1.7 ml) at room temperature and stirred at 50 °C for 9 h. Saturated aqueous NaHCO₃ solution was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:50)] to afford **4** (22.9 mg, 65%) as a colorless solid.

Entry 3. A solution of PtCl₄ (2.9 mg, 9.0 μmol) in ethanol (0.6 ml) was stirred at 50 °C. After 1 h, a solution of **3** (36.6 mg, 0.16 mmol) in ethanol (1.0 ml) was added to the mixture and stirred at 50 °C for 1 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:20)] to afford **4** (27.1 mg, 79%) as a colorless solid.

Entry 4. PtCl₄ (2.8 mg, 8.0 μmol) was added to a solution of **3** (36.9 mg, 0.16 mmol) in *tert*-butanol (1.6 ml) at room temperature and stirred at 50 °C for 24 h. Saturated aqueous NaHCO₃ solution was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:50)] to afford **4** (0.79

mg, 2%) as a colorless solid and **3** (21.5 mg, 58%) was recovered from the later fractions.

Entry 5. PtCl₂ (3.0 mg, 11.3 μmol) was added to a solution of **3** (51.1 mg, 0.227 mmol) in dichloroethane (2.3 ml) at room temperature and stirred at 50 °C for 24 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:49)] to afford **4** (4.6 mg, 10%) as a colorless solid and **3** (38.6 mg, 76%) was recovered from the later fractions.

Entry 6. PtCl₂ (4.2 mg, 15.8 μmol) was added to a solution of **3** (71.2 mg, 0.316 mmol) in ethanol (3.2 ml) at room temperature and stirred at 50 °C for 24 h. The solvent was evaporated under reduced pressure and the residue was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:49)] to afford **4** (13.3 mg, 21%) as a colorless solid and **3** (48 mg, 67%) was recovered from the later fractions.

Entry 7. A solution of PtCl₂ (5.9 mg, 22.1 μmol) in ethanol (1 ml) was stirred at 50 °C. After 1 h, a solution of **3** in ethanol (3 ml) was added to the mixture and stirred at 50 °C for 24 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:49)] to afford **4** (35.0 mg, 40%) as a colorless solid and **3** (48 mg, 48%) was recovered from the later fractions.

Experimental Procedures for Table 2.

Entry 1. A solution of PtCl₄ (2.2 mg, 7.0 μmol) in ethanol (0.3 ml) was stirred at 50 °C. After 1 h, a solution of **5** (29.0 mg, 0.13 mmol) in ethanol (1.0 ml) was added to the mixture and stirred at 50 °C for 2 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:3 to 1:1)] to afford **6** (12.7 mg, 50%) as a yellow oil and **5** (4.9 mg, 17%) was recovered from the later fractions.

Entry 2. CsCO₃ (7.3 mg, 22.5 μmol) was added to a solution of PtCl₄ (1.9 mg, 5.63 μmol) in ethanol (0.5

ml). After being stirred at 50 °C for 1 h, a solution of **5** (24.9 mg, 0.113 mmol) in ethanol (0.4 ml) was added to the mixture and stirred at 50 °C for 2 h. The solvent was evaporated under reduced pressure and the residue was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:3 to 1:1)] to recover **5** (17 mg, 68%) as a colorless oil.

Entry 3. Proton sponge® (6.3 mg, 29.6 µmol) was added to a solution of PtCl₄ (2.5 mg, 7.4 µmol) in ethanol (0.48 ml). After being stirred at 50 °C for 1 h, a solution of **5** (33.7 mg, 0.148 mmol) in ethanol (1.0 ml) was added to the mixture and stirred at 50 °C for 2 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:3 to 1:1)] to recover **5** (29.6 mg, 91%) as a colorless oil.

Entry 4. 2,6-Di-*tert*-butyl-4-methylpyridine (5.8 mg, 28 µmol) was added to a solution of PtCl₄ (2.4 mg, 7.0 µmol) in ethanol (0.4 ml) and stirred at 50 °C for 1 h. A solution of **5** (31.5 mg, 0.14 mmol) in ethanol (1.0 ml) was added to the mixture and stirred at 50 °C for 2 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:3 to 1:1)] to afford **6** (11.9 mg, 43%) as a yellow oil and **5** (13.8 mg, 44%) was recovered from the later fractions.

Entry 5. 2,6-Di-*tert*-butyl-4-methylpyridine (18.6 mg, 90 µmol) was added to a solution of PtCl₄ (7.6 mg, 22 µmol) in ethanol (1.0 ml) and stirred at 50 °C for 1 h. A solution of **5** (33.4 mg, 0.15 mmol) in ethanol (0.5 ml) was added to the mixture and stirred at 50 °C for 2 h. The solvent was evaporated under reduced pressure and the residue was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:3 to 1:1)] to afford **6** (21.1 mg, 72%) as a yellow oil.

4-(4,5,6,7-Tetrahydro-1*H*-indol-2-yl)butan-1-ol (6). IR (film, cm⁻¹) 3354, 1605, 1443, 1416, 1057, 1032, 785; ¹H-NMR (400 MHz, CDCl₃) δ 1.35 (1H, br), 1.60-1.83 (8H, m), 2.46 (2H, t, *J* = 6.4 Hz), 2.53 (2H, t, *J* = 6.2 Hz), 2.58 (2H, t, *J* = 7.2 Hz), 3.67 (2H, t, *J* = 6.2 Hz), 5.66 (1H, d, *J* = 2.4 Hz), 7.47 (1H, br); ¹³C-NMR (100 MHz, CDCl₃) δ 22.8, 22.9, 23.6, 23.9, 26.1, 27.6, 32.4, 62.8, 104.1, 116.7, 125.3, 130.4; MS *m/z* 193 (M⁺, 27.5), 134 (100); HRMS Calcd C₁₂H₁₉NO: 193.1467. Found: 193.1454.

General Procedure for Table 3.

2,6-Di-*tert*-butyl-4-methylpyridine was added to a solution of PtCl₄ in ethanol and stirred at 50 °C for 1 h. A solution of the substrate in ethanol was added to the mixture and stirred at 50 °C (for entries 1-6) or refluxed (for entries 7-9) under Ar atmosphere or aerobic condition. The reaction mixture was concentrated under reduced pressure to afford the crude product.

2-Phenyl-4,5,6,7-tetrahydro-1H-indole (4) (Entry 1). 2,6-Di-*tert*-butyl-4-methylpyridine (14.8 mg, 72 μmol), a solution of PtCl₄ (6.1 mg, 18 μmol) in ethanol (1.0 ml), and solution of **3** (88.1 mg, 0.36 mmol) in ethanol (2.6 ml) was reacted at 50 °C for 4 h according to the general procedure. The crude product was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:20)] to afford **4** (62.8 mg, 88%) as a colorless solid.

2-Pentyl-4,5,6,7-tetrahydro-1H-indole (8) (Entry 3). 2,6-Di-*tert*-butyl-4-methylpyridine (24.9 mg, 0.12 mmol), a solution of PtCl₄ (9.4 mg, 28 μmol) in ethanol (0.4 ml), a solution of **7** (41.0 mg, 0.19 mmol) in ethanol (1.5 ml) was reacted at 50 °C for 90 min according to the general procedure. The crude product was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:99)] to afford **8** (19.7 mg, 55%) as a yellow oil; IR (film, cm⁻¹) 3474, 3369, 1603, 1466, 1445, 1412, 783; ¹H-NMR (400 MHz, CDCl₃) δ 0.90 (3H, t, *J* = 6.5 Hz), 1.25-1.40 (4H, m), 1.54-1.64 (2H, m), 1.70-1.82 (4H, m), 2.46 (2H, t, *J* = 6.5 Hz), 2.50-2.55 (4H, m), 5.65 (1H, d, *J* = 2.4 Hz), 7.38 (1H, br s); ¹³C-NMR (100 MHz, CDCl₃) δ 14.1, 22.6, 22.7, 22.9, 23.6, 23.9, 27.9, 29.6, 31.8, 103.9, 116.6, 125.0, 131.1; MS *m/z* 191 (M⁺,

27.9), 134 (100), 190 (5.1); HRMS Calcd C₁₃H₂₁N: 191.1674. Found: 191.1654.

2-[4-(*tert*-Butyldiphenylsilyloxy)butyl]-4,5,6,7-tetrahydro-1*H*-indole (10) (Entry 4). 2,6-Di-*tert*-butyl-4-methylpyridine (22.4 mg, 0.11 mmol), a solution of PtCl₄ (9.2 mg, 27 μmol) in ethanol (0.4 ml), and a solution of **9** (83.4 mg, 0.18 mmol) in ethanol (1.5 ml) was reacted at 50 °C for 60 min according to the general procedure. The crude product was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:99)] to afford **10** (19.7 mg, 55%) as a yellow oil; IR (film, cm⁻¹) 3373, 1472, 1427, 1111, 702, 613; ¹H-NMR (400 MHz, CDCl₃) δ 1.05 (9H, s), 1.58-1.82 (8H, m), 2.46 (2H, t, *J* = 5.9 Hz), 2.48-2.56 (4H, m), 3.69 (2H, t, *J* = 5.9 Hz), 5.63 (1H, s), 7.33-7.43 (6H, m), 7.66 (4H, d, *J* = 6.4 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 19.3, 22.8, 23.0, 23.6, 23.9, 26.1, 27.0, 27.6, 32.3, 63.7, 104.0, 116.6, 125.1, 127.5, 129.5, 130.7, 134.0, 135.5; MS *m/z* 431 (M⁺, 37.1), 199 (100), 374 (45.4), 269 (75.5), 149 (72.1); HRMS Calcd C₂₈H₃₇NOSi: 431.2644. Found: 431.2650.

4-(4,5,6,7-Tetrahydro-1*H*-indol-2-yl)butyric Acid Ethyl Ester (12) (Entry 5). 2,6-Di-*tert*-butyl-4-methylpyridine (22.5 mg, 0.11 mmol), a solution of PtCl₄ (9.1 mg, 27 μmol) in ethanol (0.4 ml), and a solution of **11** (36.8 mg, 0.14 mmol) in ethanol (1.4 ml) was reacted at 50 °C for 60 min according to the general procedure. The residue was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:6)] to afford **12** (21.2 mg, 64%) as a yellow solid; mp 82-83 °C (yellow scaly from ethyl acetate-hexane); IR (film, cm⁻¹) 3375, 1722, 1445, 1416, 1375, 1348, 1275, 1178; ¹H-NMR (400 MHz, CD₃OD) δ 1.22 (3H, t, *J* = 7.0 Hz), 1.68-1.76 (4H, m), 1.83 (2H, quint, *J* = 7.3 Hz), 2.29 (2H, t, *J* = 7.3 Hz), 2.39 (2H, t, *J* = 6.0 Hz), 2.49 (2H, t, *J* = 7.0 Hz), 2.51 (2H, t, *J* = 7.3 Hz), 4.08 (2H, q, *J* = 7.1 Hz),

5.47 (1H, d, $J = 2.4$ Hz), 9.33 (1H, br s); ^{13}C -NMR (100 MHz, CD_3OD) δ 14.6, 23.8, 24.1, 24.9, 25.3, 26.6, 28.1, 34.5, 61.4, 104.8, 116.7, 126.4, 130.4, 175.4; MS m/z 235 (M^+ , 30.9), 134 (100), 190 (15.5); HRMS Calcd $\text{C}_{14}\text{H}_{21}\text{NO}_2$: 235.1572. Found: 235.1551; *Anal.* Calcd $\text{C}_{14}\text{H}_{21}\text{NO}_2$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.40; H, 8.94; N, 5.95.

***N*-(*tert*-butoxycarbonyl)-*p*-toluenesulfonyl-6-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)butylamide (14)**

(Entry 6). 2,6-Di-*tert*-butyl-4-methylpyridine (15.5 mg, 75.6 μmol), a solution of PtCl_4 (5.5 mg, 16 μmol) in ethanol (1.8 ml), and a solution of **13** (151 mg, 0.32 mmol) in ethanol (9.0 ml) was reacted at 50 $^\circ\text{C}$ for 30 min according to the general procedure. The crude product was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:7)] to afford **14** (97.7 mg, 69%) as a colorless amorphous; IR (film, cm^{-1}) 3406, 2924, 2851, 1730, 1354, 1258, 1153, 1088, 669; ^1H -NMR (400 MHz, C_6D_6) δ 1.10 (9H, s), 1.55-1.58 (2H, m), 1.70 (4H, m), 1.86-1.92 (5H, m), 2.36 (2H, m), 2.42 (2H, t, $J = 7.2$ Hz), 2.60 (2H, m), 3.91 (2H, t, $J = 7.2$ Hz), 5.81 (1H, s), 6.74 (2H, d, $J = 8.0$ Hz), 6.87 (1H, br s), 7.82 (2H, d, $J = 8.0$ Hz); ^{13}C -NMR (150 MHz, CD_3OD) δ 21.5, 23.7, 24.2, 24.9, 25.3, 28.1 (two peaks), 28.3, 30.7, 48.0, 85.2, 104.6, 116.7, 126.1, 129.0, 130.4, 131.1, 138.8, 145.8, 152.4; MS m/z 446 (M^+ , 34.7), 174 (67.5), 134 (100); HRMS Calcd $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_4\text{S}$: 446.2239. Found: 446.2258.

2-Phenyl-1*H*-pyrrole (16)^{S8} (Entry 7). 2,6-Di-*tert*-butyl-4-methylpyridine (25.1 mg, 120 μmol), a solution of PtCl_4 (10.3 mg, 31 μmol) in ethanol (1 ml), and a solution of **15** (35 mg, 0.20 mmol) in ethanol (19 ml) was refluxed for 6 h according to the general procedure. The crude product was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:20)] to afford **16** (21.8 mg, 74%) as a red solid; mp 129-130 $^\circ\text{C}$ (pale red plates from ethyl acetate-hexane), lit.^{S8} 128-130 $^\circ\text{C}$; IR (film, cm^{-1})

3433, 3389, 1604, 1580, 1466, 1215, 758, 719, 692; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 6.30 (1H, dd, $J = 6.0$, 2.8 Hz), 6.51-6.54 (1H, m), 6.85 (1H, m), 7.20 (1H, t, $J = 7.4$ Hz), 7.35 (2H, t, $J = 7.4$ Hz), 7.46 (2H, dd, $J = 7.4$, 1.4 Hz), 8.42 (1H, br s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 105.9, 110.0, 118.8, 123.8, 126.1, 128.8, 132.0, 132.6; MS m/z 143 (M^+ , 100), 143 (100), 115 (39.1); HRMS Calcd $\text{C}_{10}\text{H}_9\text{N}$: 143.0735. Found: 143.0752.

2-Tridecyl-1H-pyrrole-2-carboxylic Acid Ethyl Ester (18) (Entry 8). 2,6-Di-*tert*-butyl-4-methylpyridine (11 mg, 53.7 μmol), a solution of PtCl_4 (3.9 mg, 11.5 μmol) in ethanol (6.7 ml), and a solution of **17** (26.8 mg, 76.7 μmol) in ethanol (1.0 ml) was refluxed for 14 h according to the general procedure. The crude product was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:9)] to afford **18** (15 mg, 61%) as a colorless solid; mp 54-56 $^\circ\text{C}$ (colorless needles from ethyl acetate-hexane); IR (film, cm^{-1}) 3302, 2918, 2851, 1678, 1493, 1472, 1321, 1227, 1209, 1144; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 0.88 (3H, t, $J = 7.2$ Hz), 1.25-1.31 (20H, m), 1.35 (3H, t, $J = 7.1$ Hz), 1.60-1.64 (2H, m), 2.61 (2H, t, $J = 7.8$ Hz), 4.30 (2H, q, $J = 7.1$ Hz), 5.96 (1H, dd, $J = 3.0$, 3.0 Hz), 6.82 (1H, dd, $J = 3.0$, 2.4 Hz), 8.99 (1H, br s); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 14.1, 14.5, 22.7, 27.8, 29.2, 29.27, 29.34 (two peaks), 29.5, 29.61, 29.62 (two peaks), 29.7, 31.9, 60.0, 107.9, 115.8, 121.1, 138.8, 161.3; MS m/z 321 (M^+ , 63.0), 292 (22.0), 276 (15.4), 248 (50.4), 152 (100); HRMS Calcd $\text{C}_{20}\text{H}_{35}\text{NO}_2$: 321.2668. Found: 321.2656.

2,5-Diphenylpyrrole (20) (Entry 9).^{S9} 2,6-Di-*tert*-butyl-4-methylpyridine (16.9 mg, 82.1 μmol), a solution of PtCl_4 (5.9 mg, 17.6 μmol) in ethanol (1.2 ml), and a solution of **19** (29 mg, 0.117 mmol) in ethanol (10.0 ml) was refluxed for 50 min according to the general procedure. H_2O was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was

washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated. The residue was purified by silica gel column chromatography [ethyl acetate-hexane (1:9)] to afford **20** (14.7 mg, 57%) as a colorless solid; mp 142-146 °C (colorless plate from ethyl acetate-hexane), lit.^{S9} 142-144 °C; IR (film, cm⁻¹) 3456, 1460, 1076, 1053, 781, 752, 691, 665; ¹H-NMR (400 MHz, CDCl₃) δ 6.58 (2H, d, *J* = 2.4 Hz), 7.20-7.55 (10H, m), 8.57 (1H, br s); ¹³C-NMR (100 MHz, CDCl₃) 107.9, 123.7, 126.3, 128.9, 132.4, 133.0; MS *m/z* 219 (M⁺, 100); HRMS Calcd C₁₆H₁₃N: 219.1048. Found: 219.1052.

Experimental Procedure for Table 3 under Aerobic Condition.

Entry 1. 2,6-Di-*tert*-butyl-4-methylpyridine (9.5 mg, 46.1 μmol), a solution of PtCl₄ (3.9 mg, 11.5 μmol) in ethanol (1.0 ml), and solution of **3** (52 mg, 0.23 mmol) in ethanol (1.3 ml) was reacted at 50 °C for 60 min according to the general procedure. The crude product was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:29)] to afford **4** (35.3 mg, 78%) as a colorless solid.

Entry 3. 2,6-Di-*tert*-butyl-4-methylpyridine (14.2 mg, 69.2 μmol), a solution of PtCl₄ (5.8 mg, 17.3 μmol) in ethanol (0.5 ml), and solution of **7** (25.3 mg, 0.12 mmol) in ethanol (0.7 ml) was reacted at 50 °C for 80 min according to the general procedure. The crude product was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:29)] to afford **8** (5.2 mg, 24%) as a yellow oil.

Entry 6. 2,6-Di-*tert*-butyl-4-methylpyridine (4.8 mg, 23.3 μmol), a solution of PtCl₄ (2.0 mg, 5.8 μmol) in ethanol (1.16 ml), and solution of **13** (55 mg, 0.116 mmol) in ethanol (2.72 ml) was reacted at 50 °C for 60 min according to the general procedure. The crude product was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:7)] to afford **14** (11.7 mg, 23%) as a colorless amorphous and **13** (7.9 mg, 14%) was recovered from the later fractions.

Entry 7. 2,6-Di-*tert*-butyl-4-methylpyridine (27.1 mg, 0.13 mmol), a solution of PtCl₄ (11.1 mg, 32.9 μmol) in ethanol (2.0 ml), and solution of **15** (37.6 mg, 0.22 mmol) in ethanol (20 ml) was refluxed at for 160 min according to the general procedure. The crude product was purified by aluminum oxide column chromatography [ethyl acetate-hexane (1:19)] to afford **16** (22 mg, 70%) as a red solid and **15** (1.2 mg, 3%) was recovered from the later fractions.

Entry 9. 2,6-Di-*tert*-butyl-4-methylpyridine (9.2 mg, 44.9 μmol), a solution of PtCl₄ (3.8 mg, 11.2 μmol) in ethanol (1.0 ml), and solution of **19** (18.5 mg, 74.8 μmol) in ethanol (6.5 ml) was refluxed for 80 min according to the general procedure. The crude product was purified by silica gel column chromatography [ethyl acetate-hexane (1:29)] to afford **20** (10.7 mg, 65%) as a colorless solid and **19** (5.7 mg, 31%) was recovered from the later fractions.

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¹³C-NMR

15

¹H-NMR

16