EXPERIMENTAL

General

^{1}H NMR and ^{13}C NMR were recorded on a Bruker AF-400 or AF-500 spectrometer. ^{1}H NMR and ^{13}C NMR data are reported in parts per million (δ) downfield from tetramethylsilane. The following abbreviations are used for the resonance patterns: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

The infrared (IR) spectra were recorded on a Nicolet 510FT-IR spectrometer as a liquid film (neat) on NaCl pellet and reported in wave numbers (cm^{-1}). Melting points (mp) were obtained on a Thomas capillary melting point apparatus and are uncorrected. High resolution EI or FAB mass spectra (MS) were recorded on a VG Autospec by the UCLA Mass Spectrometry Staff and are reported in *m/z* units for the most abundant peaks. Optical rotations were recorded at room temperature on Perkin-Elmer 243 or 241 MC Polarimeters. Circular dichroism was recorded on JASCO PS-150J Spectropolarimeter. Flash chromatography was carried out in the indicated solvents on E. Merck silica gel 60 (230-400 mesh). Concentration or evaporation of solvent refers to removal of solvent under reduced pressure by using a rotary evaporator and a Cole-Parmer aspirator pump.

The following solvents and reagents were distilled from the indicated agent under dry argon: tetrahydrofuran (THF), and diethyl ether from sodium benzophenone ketyl; dichloromethane (CH_2Cl_2), diisopropylamine, and triethylamine (Et_3N) from calcium hydride. All other reagents were purified by literature procedures.

All reactions were performed under an inert atmosphere of argon.

(4*S*,5*S*)- 4,5-Dihydro-2-methyl-4,5-diphenyl-1*H*-imidazole (9).

Acetylamidine hydrochloride (4.0 g, 42 mmol) was dissolved in 100 mL MeOH at 0 °C, then NaOH (1.7 g, 42 mmol) was added. After it had stirred for 2 h, the reaction mixture was filtered, dried over $MgSO_4$, and concentrated under vacuum to give acetylamidine (2.0 g, 35 mmol) as a colorless oil. Acetylamidine was then diluted with 6 mL dry DMF and dried with 1 g of 4 Å molecular sieves for 30 min. The dried acetylamidine in DMF was mixed with (*R*, *R*)-stilbenediol cyclic sulfate **8**[1] (2.8 g, 10 mmol) and 60 mL dry toluene and the reaction was refluxed overnight. Concentration of the reaction mixture gave a gummy orange residue. Flash column chromatography of the residue (silica gel, ethyl acetate with trace of Et_3N) afforded the desired product **9** (1.28 g, 54%) as a yellow oil, which crystallized after storage at room temperature for one week.

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[1]Oi, R.; Sharpless, K. B. *Tetrahedron Lett.* **1991**, *32*, 999.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.13-7.47 (10H, m), 6.28 (1H, bs), 4.57 (2H, s), 1.82 (3H, s).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 163.50, 143.87, 128.57, 127.28, 126.57, 75.00, 14.91.

IR (neat): 3152, 3063, 3005, 2874, 1603, 1495, 1454, 1277, 1026, 760 cm^{-1}.

High Resolution MS (FAB, *m/z*): 237.1392 $(M+H)^+$, calculated for $C_{16}H_{17}N_2$ 237.1392.

mp 79 °C.

$[\alpha]_D^{25}$ = -153.1° (c = 18.8, CH_2Cl_2).

(4S,5S)- 4,5-Dihydro-1,2-dimethyl-4,5-diphenyl-1*H*-imidazole (10).
n-Butyllithium (1.15 mL, 1.5 M in hexane, 1.72 mmol) was added to imidazoline **9** (0.3685 g, 1.56 mmol) in 25 mL THF at -78 °C. The mixture was stirred for 2 min and methyl iodide (0.145 mL, 1.56 mmol) in 1 mL THF was added dropwise. The reaction was stirred for 30 min and allowed to slowly warm up to room temperature. Concentration of the reaction mixture gave a slightly yellow oily residue. Flash column chromatography of the residue (silica gel, ethyl acetate with a trace of Et_3N) afforded the desired product **10** (0.3873 g, 99%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.16-7.31 (10H, m), 4.75 (1H, d, *J* = 10.2 Hz), 4.14 (1H, d, *J* = 10.2 Hz), 2.61 (3H, s), 2.09 (3H, s).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 164.31, 143.42, 140.88, 128.79, 128.38, 127.83, 127.18, 127.04, 126.94, 77.66, 77.35, 32.39, 14.69.

IR (neat): 3362, 3086, 3030, 1616, 1583, 1495, 1454, 1404 cm^{-1}.

High Resolution MS (EI, *m/z*): 250.1464 (M+), calculated for $C_{17}H_{18}N_2$ 250.1470.

$[\alpha]_D^{25}$ = -21.7° (c = 6.0, CH_2Cl_2).

(4*S*,5*S*)-4,5-Dihydro-2[3-([(1,1-dimethylethyl)dimethylsilyloxy]propyl)]-1-methyl-4,5-diphenyl-1*H*-imidazole (11).
n-Butyllithium (1.90 mL, 2.18 M in hexane, 4.15 mmol) was added to imidazole **10** (0.9436 g, 3.77 mmol) in 25 mL THF at -78 °C. The mixture was stirred for 2 min and 2-iodoethoxyl TBS

ether (1.078 g, 3.77 mmol) in 1 mL THF was added dropwise. The reaction was stirred for 30 min and then allowed to slowly warm up to room temperature. Concentration of the reaction mixture gave a slightly yellow oily residue. Flash column chromatography of the residue (silica gel, hexane : ethyl acetate : Et_3N = 3 : 1 : trace) afforded the desired product **11** (1.428 g, 93%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.17-7.36 (10H, m), 4.76 (1H, d, J = 9.9 Hz), 4.14 (1H, d, J = 9.9 Hz), 3.80 (2H, t, J = 6.0 Hz), 2.68 (3H, s), 2.51 (2H, t, J = 7.4 Hz), 2.00-2.05 (2H, m), 0.93 (9H, s), 0.09 (6H, s).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.14, 143.78, 141.20, 128.76, 128.34, 127.74, 127.15, 126.98, 126.94, 77.83, 77.40, 62.48, 32.17, 29.70, 26.00, 24.46, 18.38, -5.25.

IR (neat): 3063, 3030, 2955, 2856, 1616, 1495, 1454, 1255, 1101, 837 cm^{-1}.

High Resolution MS (EI, *m/z*): 409.2665 $(M+H)^+$, calculated for $C_{25}H_{37}N_2OSi$ 409.2675.

$[\alpha]_D^{25}$ = -3.5° (c = 12.9, CH_2Cl_2).

(4*S*,5*S*)-4,5-Dihydro-1,3-dimethyl-2-[3-([(1,1-dimethylethyl)dimethylsilyloxy] propyl)]-4,5-diphenyl-3*H*-imidazolium iodide (12).

Imidazole **11** (20 mg, 0.08 mmol) was dissolved in 2 mL dry THF and the mixture was cooled in an ice bath. Methyl iodide (0.025 mL, 0.40 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 2 h. Removal of the solvent under reduced pressure afforded a quantitative yield of **12** as a white solid. This crude product was not further purified and was used directly for the next step.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.05-7.40 (10H, m), 4.99 (2H, s), 3.82 (2H, t, J = 5.3 Hz), 3.36 (1H, dt, J = 14.8, 7.2 Hz), 3.12 (6H, s), 3.10 (1H, dt, J = 14.8, 7.2 Hz), 1.97-2.06 (2H, m), 0.88 (9H, s), 0.07 (6H, s).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.52, 134.05, 129.95, 129.65, 128.45, 75.06, 61.28, 33.19, 29.00, 25.95, 24.01, 18.30, -5.21.

IR (CH_2Cl_2 film): 3063, 3003, 2955, 2883, 1610, 1456, 1253, 1093, 837 cm^{-1}.

High Resolution MS (FAB, *m/z*): 422.2762 $(M\text{-}HI)^+$, calculated for $C_{26}H_{38}N_2OSi$ 422.2753.

$[\alpha]_D^{25}$ = -86.2° (c = 1.03, CH_2Cl_2).

(4*S*,5*S*)-1,3-Dimethyl-2-[3-([(1,1-dimethylethyl)dimethylsilyloxy]propyl)]-4,5-diphenyl-2-ethynylimidazolidine (13).
Imidazolium iodide **12** (0.4903 g, 1.151 mmol) was suspended in 2 mL of dry THF at -78 °C under argon. Lithium (trimethylsilyl)acetylide (1.72 mL, 1.0 M in THF, 1.72 mmol) was added dropwise. The resulting yellow solution was warmed to room temperature and stirred for 0.5 h. The reaction was quenched with water, extracted with CH_2Cl_2, and dried over Na_2SO_4. Concentration gave a yellow oil, which was diluted in 2 mL dry THF and then treated with Bu_4NF (0.9 mL, 1 M in THF, 0.90 mmol). After the mixture stirred for 5 min, it was washed with water and extracted with CH_2Cl_2. The organic layer was separated and dried over Na_2SO_4. Concentration of this solution gave a yellow oily residue. Flash column chromatography of the residue (silica gel, hexane : ethyl acetate : Et_3N = 10 : 1 : trace) afforded the desired product **13** (0.4411 g, 85%) as a yellow oil.

^1H NMR ($CDCl_3$, 400 MHz) δ: 7.17-7.33 (10H, m), 3.86 (1H, d, *J* = 8.2 Hz), 3.73-3.77 (2H, m), 3.62 (1H, d, *J* = 8.2 Hz), 2.70 (1H, s), 2.30 (3H, s), 2.28 (3H, s), 1.96-2.00 (3H, m), 1.77-1.79 (1H, m), 0.97 (9H, s), 0.13 (6H, s).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 139.80, 139.41, 128.85, 128.37, 128.00, 127.95, 127.40, 127.37, 84.18, 80.49, 76.81, 75.23, 73.59, 63.41, 35.02, 33.69, 31.86, 27.10, 26.06, 18.43, -5.15.

IR (neat): 3302, 3063, 3030, 2945, 2843, 2799, 1603, 1495, 1456, 1165, 1095 cm^{-1}.

High Resolution MS (FAB, *m/z*): 447.2832 $(M\text{-}H)^+$, calculated for $C_{28}H_{39}N_2OSi$ 447.2832.

$[\alpha]_D^{25}$ = -41.0° (c = 2.18, CH_2Cl_2).

(4*S*,5*S*)-2-Ethenyl-1,3-dimethyl-4,5-diphenylimidazolidine-2-propanol.
Acetylene **13** (0.6234 g, 1.39 mmol) and 74.8 mg 5% $Pd/BaSO_4$ were stirred in 65 mL ethyl acetate and 6.5 mL pyridine under an atmosphere of hydrogen gas for 30 min. Filtration of the mixture, followed by concentration of the filtrate gave a yellow residue, which was dissolved in 65 mL dry THF along with 2.8 mL Bu_4NF (1M in THF, 2.8 mmol). After the mixture was stirred

overnight, the reaction was quenched with water and extracted with CH_2Cl_2. The organic layer was separated and dried over Na_2SO_4. Concentration of this solution gave a yellow oily residue. Flash column chromatography of the residue (silica gel, hexane : ethyl acetate : Et_3N = 3 : 1 : trace) afforded the desired product (0.4411g, 98%) as a yellow oil.

^1H NMR ($CDCl_3$, 400 MHz) δ: 7.10-7.25 (10H, m), 5.96 (1H, dd, *J* = 17.3, 10.4 Hz), 5.61 (1H, dd, *J* = 17.3, 2.0 Hz), 5.37 (1H, dd, *J* = 10.4, 2.0 Hz), 3.97 (1H, d, *J* = 8.6 Hz), 3.81-3.86 (1H, m), 3.68-3.76 (1H, m), 3.50 (1H, d, *J* = 8.6 Hz), 3.48 (1H, bt, *J* = 5.4 Hz), 2.25 (3H, s), 2.17 (3H, s), 2.06-2.13 (1H, m), 1.93-1.96 (2H, m), 1.86-1.91 (1H, m).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 140.37, 139.82, 138.73, 128.35, 128.16, 128.11, 128.02, 127.56, 127.44, 115.25, 81.26, 76.27, 74.73, 63.69, 34.58, 32.38, 31.59, 27.74.

IR (neat): 3330, 3030, 3063, 2944, 2845, 2793, 1603, 1495, 1452, 1172 cm^{-1}.

High Resolution MS (FAB, *m/z*): 337.2280 $(M+H)^+$, calculated for $C_{22}H_{29}N_2O$ 337.2280.

$[\alpha]_D^{25}$ = -22.9° (c = 3.14, CH_2Cl_2).

(4*S*,5*S*)-2-Ethenyl-1,3-dimethyl-4,5-diphenylimidazolidine-2-propanal (14). Oxalyl chloride (21 μL, 0.24 mmol) was added to a solution of dimethyl sulfoxide (34.4 μL, 0.488 mmol) in 6 mL of dry CH_2Cl_2 at -78 °C under argon. After the mixture was stirred for 15 min, a solution of the above alcohol (74.6 mg, 0.22 mmol) in 1 mL dry CH_2Cl2 was added dropwise. The reaction was stirred for 45 min, quenched with Et_3N (0.30 mL, 2.1 mmol) and warmed to room temperature. Concentration of the reaction mixture, followed by column chromatography of the residue (silica gel, hexane : ethyl acetate : Et_3N = 1 : 5 : trace), gave 73.5 mg (100%) of the aldehyde **14** as a colorless oil, which was stored at -20 °C to avoid decomposition.

^1H NMR ($CDCl_3$, 400 MHz) δ: 9.91 (1H, t, *J* = 1.8 Hz), 7.03-7.27 (10H, m), 5.96 (1H, dd, *J* = 17.3, 10.5 Hz), 5.57 (1H, dd, *J* = 17.3, 1.8 Hz), 5.38 (1H, dd, *J* = 10.5, 1.8 Hz), 3.86 (1H, d, *J* = 8.5 Hz), 3.50 (1H, d, *J* = 8.5 Hz), 2.95 (1H, dtd, *J* = 17.2, 7.2, 2.0 Hz), 2.61 (1H, dtd, *J* = 17.2, 6.1, 1.4 Hz), 2.31-2.39 (1H, m), 2.21(3H, s), 2.09 (3H, s), 2.06-2.14 (1H, m).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 202.41, 139.92, 139.57, 138.66, 128.16 (2 carbons), 128.12, 128.11 (2 carbons), 127.51, 115.52, 80.80, 76.06, 74.83, 39.50, 34.14, 31.42, 27.24.

IR (neat): 3086, 3063, 2945, 2843, 2795, 2720, 1720, 1603, 1495, 1452, 1165 cm^{-1}.

High Resolution MS (FAB, *m/z*): 335.2123 $(M+H)^+$, calculated for $C_{22}H_{27}N_2O$ 335.2123.

$[\alpha]_D^{25}$ = -18.1° (c = 3.41, CH_2Cl_2).

(4'*S*,5'*S*)-1',3'-Dimethyl-4',5'-diphenyl-3,3a*R*,4,5,6a*R*-hexahydro-1-phenylmethylspiro[1*H*-cyclopent[*c*]isoxazole-4,2'-imidazolidine] (18) and (4'*S*,5'*S*)-1',3'-Dimethyl-4',5'-diphenyl-3,3a*S*,4,5,6a*S*-hexahydro-1-phenylmethylspiro[1*H*-cyclopent[*c*]isoxazole-4,2'-imidazolidine] (19).

To *N*-(phenylmethyl)hydroxylamine (98.6 mg, 0.795 mmol) was added the aldehyde **14** (0.2656 g, 0.795 mmol), 15 mL of toluene and molecular sieves 4 Å (0.2 g). The mixture was then refluxed for 20 h. The solid was filtered and the filtrate was concentrated to give a yellow oily residue. ^1H NMR analysis showed that two products were formed in a ratio about 1 : 1.2. Flash column chromatography of the residue (silica gel, hexane : ethyl acetate : Et_3N = 15 : 1 : trace) afforded product **19** (0.2004 g, 57%) as a white solid and product **18** (0.096 g, 34%) as a yellow oil.

Imidazolidine (19)

^1H NMR ($CDCl_3$, 400 MHz) δ: 7.09-7.48 (15H, m), 4.50 (1H, dd, *J* = 9.0, 5.0 Hz), 4.31 (1H, dd, *J* =8.9, 9.0 Hz), 4.12 (1H, d, *J* =12.9 Hz), 3.92 (1H, d, *J* = 12.9 Hz), 3.61 (1H, d, *J* = 8.7 Hz), 3.61-3.63 (1H, m), 3.41-3.46 (1H, m), 3.37 (1H, d, *J* = 8.7 Hz), 2.48-2.57 (2H, m), 2.45 (3H, s), 2.22 (3H, s), 2.06-2.09 (1H, m), 1.82-1.91 (1H, m).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 140.62, 139.20, 137.64, 129.15, 128.48 (2 carbons), 128.25, 128.08, 127.73, 127.63, 127.40, 127.33, 90.93, 77.97, 75.15, 70.10, 68.18, 60.82, 51.27, 36.72, 33.64, 33.50, 30.46.

IR (neat): 3086, 3028, 2947, 2847, 2793, 1603, 1495, 1452, 1321, 1265, 1028 cm^{-1}.

mp 117 °C.

High Resolution MS (FAB, *m/z*): 439.6006 $(M)^+$, calculated for $C_{29}H_{33}N_3O$ 439.2623.

$[\alpha]_D^{25}$ = +31.6° (c = 1.60, CH_2Cl_2).

Imidazolidine (18)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.31-7.46 (15H, m), 4.19 (1H, dd, *J* = 8.8, 8.8 Hz), 4.07 (1H, dd, *J* = 7.1, 8.4 Hz), 4.03 (1H, d, *J* = 12.8 Hz), 3.89-3.90 (1H, m), 3.87 (1H, d, *J* = 12.8 Hz), 3.79 (1H, dd, *J* = 7.8 Hz), 3.74 (1H, d, *J* = 7.8 Hz), 3.30 (1H, ddd, *J* = 7.4, 7.3, 7.4 Hz), 2.45 (3H, s), 2.28 (3H, s), 2.10-2.18 (1H, m), 2.00-2.06 (1H, m), 1.82-1.88 (1H, m), 1.76-1.79 (1H, m).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 142.53, 141.07, 137.47, 129.23, 128.86, 128.46, 128.32, 128.29, 127.47, 127.42, 127.22, 127.12, 92.91, 76.52, 76.35, 69.71, 67.40, 61.63, 54.93, 37.84, 36.22, 29.29, 27.01.

IR (neat): 3086, 3024, 2949, 2868, 2791, 1601, 1493, 1452, 1348, 1261, 1016 cm^{-1}.

$[\alpha]_D^{25}$ = -59.1° (c = 4.70, CH_2Cl_2).

High Resolution MS (FAB, *m/z*): 439.6006 $(M)^+$, calculated for $C_{29}H_{33}N_3O$ 439.2623.

3aβ,6aβ-1-Phenylmethylhexahydrocyclopenta[*c*]isoxazol-4-one (21).

To a solution of the aminal **19** (7.0 mg, 0.016 mmol) in 1.5 mL THF was added dropwise 1 mL 1N HCl. The reaction mixture was stirred vigorously for 15 min before being extracted with CH_2Cl_2 (3 x 1 mL). The organic layers were dried over Na_2SO_4 and concentrated to give the ketone **21** as a light yellow oily residue (3.2 mg, 93%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.03-7.44 (5H, m), 4.26 (1H, dd, *J* = 9.1, 9.0 Hz), 4.04 (2H, s), 3.96 (1H, dd, *J* = 8.6, 4.2 Hz), 3.72 (1H, bm), 3.28 (1H, m), 2.65 (1H, ddd, *J* = 18.4, 9.2, 9.1 Hz), 2.36 (1H, dddd, *J* = 13.7, 9.1, 4.7, 1.5 Hz), 2.21 (1H, dddd, *J* = 13.7, 9.1, 6.2, 2.9 Hz), 2.01 (1H, m).

IR (neat): 3063, 3030, 2941, 2878, 1738, 1606, 1496, 1454, 1157, 1028 cm^{-1}.

^{13}C NMR ($CDCl_3$, 126 MHz) δ: 218.19, 136.62, 128.72, 128.33, 127.45, 68.41, 68.06, 60.12, 56.13, 36.61, 30.19.

$[\alpha]_D^{25}$ = +277.5° (c = 1.60, CH_2Cl_2).

High Resolution MS (FAB, *m/z*): 217.2574 (M^+), calculated for $C_{13}H_{15}NO_2$ 217.1103.

3aα,6aα-1-Phenylmethylhexahydrocyclopenta[*c*]isoxazol-4-one (20).
Application of the above procedure to **18** gave the ketone **20** in 93% yield, whose ^1H NMR, ^{13}C NMR, and IR spectra are identical to the spectra of **21**.

$[\alpha]_D$ = -245.2° (c = 1.50, CH_2Cl_2).

(4*S*,5*S*)-2-Ethenyl-1,3-dimethyl-4,5-diphenylimidazolidine-2-propanal 4-methylphenylsulfonylhydrazone.
To a solution of the aldehyde **14** (28.7 mg, 0.086 mmol) in 1 mL of dry THF was added *p*-tosylhydrazine (18.1 mg, 0.095 mmol) along with 4 Å molecular sieves (0.5 g) at -78 °C. After being stirred for 30 min, the reaction mixture was allowed to warm up to room temperature and the molecular sieves were filtered. Concentration of the filtrate gave a clear oil (43.2 mg, 100%). This crude product, consisted of *E* and Z isomers (*E*/*Z* = 4 : 1), was used for the next step without further purification. Although the *E* and *Z* isomers are not separable via column chromatography, it is possible to analyze the major one by NMR.

E-isomer:
^1H NMR ($CDCl_3$, 500 MHz) δ: 7.88-7.89 (2H, d, *J* = 8.4 Hz), 7.39 (1H, d, *J* = 5.6 Hz), 7.08-7.35 (12H, m), 5.86 (1H, dd, *J* = 17.3, 10.5 Hz), 5.48 (1H, dd, *J* = 17.3, 1.8 Hz), 5.33 (1H, dd, *J* = 10.5, 1.8 Hz), 3.78 (1H, d, *J* = 8.4 Hz), 3.48 (1H, d, *J* = 8.4 Hz), 2.81-2.86 (1H, m), 2.46 (3H, s), 2.17 (3H, s), 2.07 (3H, s), 1.96-2.01 (2H, m), 1.88-1.91 (1H, m).

^{13}C NMR ($CDCl_3$, 126 MHz) δ: 153.54, 143.93, 139.94, 139.53, 139.11, 135.26, 129.84, 129.54, 129.47, 128.17, 127.98, 127.71, 127.47, 127.30, 115.02, 80.64, 75.90, 74.86, 34.15, 31.39, 30.94, 30.69, 21.48.

IR (neat): 3209, 3086, 3030, 2943, 2845, 2795, 2253, 1633, 1599, 1495, 1452, 1273, 1174, 1001, 700 cm^{-1}.

High Resolution MS (FAB, *m/z*): 503.2495 $(M+H)^+$, calculated for $C_{29}H_{35}N_4O_2S$ 503.2480.

1',3'-Dimethyl-4'*S*,5'*S*-diphenyl-3,3a*S*,4,5,6,6a*S*-hexahydrospiro[cyclopenta-pyrazole-4,2'-imidazolidine] (16).

The crude hydrazone from above (18.3 mg, 0.036 mmol) and potassium *t*-butoxide (6.2 mg, 0.047 mmol) were dissolved in 1.5 mL toluene-d_8. The mixture was then immersed in an oil bath (50 °C) for 5 h. The mixture was washed with water and the organic layer was dried over Na_2SO_4. Evaporation of the solvent gave a light yellow oily residue which was purified by flash column chromatography (silica gel, hexane : ethyl acetate : Et_3N = 7 : 1 : trace) to afford the desired product **16** (10.6 mg, 84% overall) as a white solid. Recrystallization of the solid from ether and hexane gave colorless needle-like crystals, whose structure was elucidated by x-ray crystallography.

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.09-7.31 (10H, m), 5.34 (1H, ddd, *J* = 18.4, 5.7, 2.8 Hz), 5.06 (1H, ddd, *J* = 11.2, 8.9, 2.5 Hz), 4.54 (1H, ddd, *J* = 18.4, 9.8, 2.0 Hz), 3.58 (1H, d, *J* = 8.8 Hz), 3.35 (1H, d, *J* = 8.8 Hz), 2.76 (1H, ddd, *J* = 11.2, 8.9, 2.8 Hz), 2.36-2.49 (2H, m), 2.23 (3H, s), 2.18 (3H, s), 1.91-1.96 (1H, m), 1.83-1.88 (1H, m).

^{13}C NMR ($CDCl_3$, 126 MHz) δ: 140.00, 138.89, 128.20, 128.04, 127.93, 127.49, 127.20 (2 carbons), 92.30, 91.15, 80.18, 77.66, 74.91, 38.19, 36.70, 34.12, 32.46, 26.95.

mp 116 °C.

IR (CH_2Cl_2 film): 3063, 3030, 2955, 2849, 2795, 2241, 1603, 1552, 1495, 1452, 1263, 1151, 700 cm^{-1}.

$[\alpha]_D^{25}$ = -32.7° (c = 0.2, CH_2Cl_2).

High Resolution MS (FAB, *m/z*): 347.2236 $(M+H)^+$, calculated for $C_{22}H_{27}N_4$ 347.2236.

1',3'-Dimethyl-4'*S*,5'*S*-diphenyl-1,3a*S*,4,5,6,6a*S*-hexahydrospiro[cyclopenta-pyrazole-4,2'-imidazolidine] (i).

The hydrazone from above (19.1 mg, 0.038 mmol) and potassium *t*-butoxide (6.5 mg, 0.049 mmol) were dissolved in 2 mL toluene. The mixture was then immersed in an oil bath (60 °C) for 20 h. The solvent was removed to give the dihydropyrazole **i** as the only product. Attempts to further purify this product via chromatography failed.

^{1}H NMR (toluene-d8, 500 MHz) δ: 7.05-7.17 (10H, m), 7.02 (1H, bs), 6.88 (1H, d, *J* = 1.8 Hz), 3.65 (1H, bddd, *J* = 12.9, 10.1, 6.2 Hz), 3.49 (1H, d, *J* = 8.7 Hz), 3.46 (1H, bd, *J* = 10.1

Hz), 3.38 (1H, d, J = 8.7 Hz), 2.10 (3H, s), 2.06-2.06 (1H, m), 1.99 (3H, s), 1.72-1.80 (1H, m), 1.51-1.62 (1H, m), 1.32-1.38 (1H, m).

^{13}C NMR (toluene-d, 500 MHz) δ: 144.28, 144.25, 140.74, 140.12, 137.62 (2 carbons), 128.87, 128.78, 128.66, 93.46, 78.26, 76.93, 61.52, 57.65, 35.81, 34.91, 34.01, 33.57.

(4*S*,5*S*)-(*E*)-Ethyl 5-(2-ethenyl-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)pent-2-enoate (22).

The aldehyde **14** (19.5 mg, 0.058 mmol) in 2 mL methylene chloride was added to (carbethoxymethylene)triphenylphosphorane (83.0 mg, 0.24 mmol) suspended in 5 mL methylene chloride at room temperature. The mixture was stirred overnight. Removal of the solvent followed by flash column chromatography (silica gel, hexane : Et_3N = 1 : trace) gave the ester **15A** as a colorless oil (23.5 mg, 100%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.10-7.26 (11H, m), 5.97 (1H, dd, J = 9.5, 1.3 Hz), 5.92 (1H, dd, J = 17.3, 10.5 Hz), 5.5 (1H, dd, J = 17.3, 1.8 Hz), 5.33 (1H, dd, J = 10.5, 1.7 Hz), 4.25 (2H, q, J = 7.1 Hz), 3.76 (1H, d, J = 8.4 Hz), 3.49 (1H, d, J = 8.4 Hz), 2.78-2.84 (1H, m), 2.40-2.43 (1H, m), 2.19 (3H, s), 2.14 (3H, s), 1.94-2.00 (1H, m), 1.85-1.90 (1H, m), 1.33 (3H, t, J = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 126 MHz) δ: 166.81, 149.93, 140.19, 139.70, 139.40, 128.12, 128.02, 128.00, 127.94, 127.39, 127.34, 120.94, 115.03, 80.84, 76.09, 75.08, 60.15, 34.43, 33.27, 31.46, 27.75, 14.30.

IR (CH_2Cl_2 film): 3348, 3030, 2978, 2870, 2795, 1716, 1653, 1495, 1367, 1267, 978 cm^{-1}.

$[\alpha]_D^{25}$ = -44.2° (c = 1.1, CH_2Cl_2).

(4*S*,5*S*)-(*E*)-5-(2-Ethenyl-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)pent-2-en-1-ol.

Diisobutylaluminum hydride (81.4 μL, 1M in hexane, 0.084 mmol) was added to the ester **22** (14.9 mg, 0.037 mmol) in 3 mL THF at -78 °C. The reaction mixture was stirred for 15 min, then it was warmed to room temperature. The mixture was quenched with 1 mL water and 3 mL of potassium sodium tartrate (aq., 1M) was added. The reaction mixture was vigorously stirred until it turned clear. The mixture was extracted with CH_2Cl_2 (3 x 5 mL), and the combined organic layers were concentrated to give an oily residue. Flash column chromatography of the residue

(silica gel, hexane : ethyl acetate : Et_3N = 1 : 3 : trace) gave the primary alcohol as a colorless oil (13.1 mg, 100%).

^1H NMR ($CDCl_3$, 500 MHz) δ: 7.14-7.31 (10H, m), 5.98 (1H, dd, *J* = 17.3, 10.5 Hz), 5.91 (1H, m), 5.85 (1H, m), 5.56 (1H, dd, *J* = 17.3, 1.9 Hz), 5.36 (1H, dd, *J* = 10.5, 2.0 Hz), 4.21 (2H, d, *J* = 5.6 Hz), 3.80 (1H, d, *J* = 8.4 Hz), 3.52 (1H, d, *J* = 8.4 Hz), 2.65-2.74 (1H, m), 2.26-2.38 (1H, m), 2.23 (3H, s), 2.18 (3H, s), 1.93-1.99 (1H, m), 1.82-1.88 (1H, m), 1.08 (1H, bs).

^{13}C NMR ($CDCl_3$, 500 MHz) δ: 140.53, 139.91, 139.67, 133.97, 128.62, 128.15, 128.01, 127.98, 127.94, 127.32, 127.26, 114.74, 80.91, 76.13, 75.15, 63.91, 34.55, 34.46, 31.33, 27.60.

IR (neat): 3348, 3030, 2941, 2845, 2795, 1603, 1495, 1452, 1273, 1072, 970 cm^{-1}.

High Resolution MS (FAB, *m/z*): 363.2433 $(M+H)^+$, calculated for $C_{24}H_{31}N_2O$ 363.2436.

$[\alpha]_D^{25}$ = -35.3° (c = 0.4, CH_2Cl_2).

(4*S*,5*S*)-(*E*)-5-(2-Ethenyl-1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)pent-2-en-1-al.

The bove alcohol (11.0 mg, 0.030 mmol) was oxidized to the corresponding aldehyde (10.9 mg, 100%) under the Swern conditions as described for the formation of compound **14**.

^1H NMR ($CDCl_3$, 500 MHz) δ: 9.58 (1H, d, *J* = 7.9 Hz), 7.07-7.26 (10H, m), 7.00-7.07 (1H, m), 6.28 (1H, ddt, *J* = 15.6, 7.9, 1.4 Hz), 5.94 (1H, dd, *J* = 17.2, 10.5 Hz), 5.53 (1H, dd, *J* = 17.3, 1.8 Hz), 5.36 (1H, dd, *J* = 10.5, 1.8 Hz), 3.78 (1H, d, *J* = 8.4 Hz), 3.50 (1H, d, *J* = 8.4 Hz), 2.91-3.00 (1H, m), 2.50-2.59 (1H, m), 2.20 (3H, s), 2.14 (3H, s), 1.88-2.06 (2H, m).

^{13}C NMR ($CDCl_3$, 500 MHz) δ: 194.16, 159.68, 140.02, 139.58, 139.26, 132.68, 128.13, 128.10 (2 carbons), 128.07, 127.94, 127.46, 115.28, 80.86, 76.10, 75.07, 34.47, 33.10, 31.48, 28.42.

IR (Neat): 3032, 2963, 2851, 2799, 2731, 1695, 1635, 1495, 1456, 1273, 947 cm^{-1}.

$[\alpha]_D^{25}$ = -27.5° (c = 0.4, CH_2Cl_2).

(4*S*,5*S*)-(*E*)-2-Ethenyl-2-(hexa-3,5-dien-1-yl)-1,3-dimethyl-4,5-diphenyl-imidazolidine (23)

To a suspension of methyltriphenylphosphonium bromide (0.146 g, 0.409 mmol) in 8 mL of dry THF at -78 °C was added *n*-butyllithium (0.135 mL, 0.327 mmol). To the resulting yellow solution was added the above aldehyde (29.4 mg, 0.0817 mmol) in 1 mL of dry THF. The cooling bath was removed and stirring was continued for 1 h. The reaction was quenched with 2 mL of water, and then extracted with CH_2Cl_2 (3 x 3 mL). The combined organic layers were concentrated to give an oily residue. Flash column chromatography of the residue (silica gel, hexane : ethyl acetate : Et_3N = 1 : 3 : trace) afforded the diene **23** (25.7 mg, 94% overall) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.15-7.30 (10H, m), 6.47 (1H, ddd, *J* = 17.0, 10.3, 6.8 Hz), 6.28 (1H, dd, *J* = 15.1, 10.4 Hz), 5.99 (1H, dd, *J* = 17.3, 10.5 Hz), 5.93 (1H, dt, *J* = 15.2, 6.9 Hz), 5.58 (1H, dd, *J* = 17.0, 1.9 Hz), 5.37 (1H, dd, *J* = 10.3, 2.0 Hz), 5.22 (1H, bd, *J* = 17.3 Hz), 5.06 (1H, bd, *J* = 10.5 Hz), 3.78 (1H, d, *J* = 8.4 Hz), 3.53 (1H, d, *J* = 8.4 Hz), 2.70-2.78 (1H, m), 2.30-2.40 (1H, m), 2.25 (3H, s), 2.19 (3H, s), 2.01(1H, ddd, *J* = 14.0, 7.2, 4.9 Hz), 1.91 (1H, ddd, *J* = 14.0, 7.2, 4.4 Hz).

^{13}C NMR ($CDCl_3$, 126 MHz) δ: 140.56, 139.67, 137.36, 135.91, 130.69, 128.15 (2 carbons), 128.03 (2 carbons), 128.00, 127.95, 127.31, 127.26, 114.71, 80.93, 76.12, 75.17, 34.54, 34.44, 31.56, 27.97.

IR (CH_2Cl_2 film): 3084, 3028, 2943, 2845, 2793, 1651, 1603, 1495, 1452, 1273, 1174, 1001, 700 cm^{-1}.

$[\alpha]_D^{25}$ = -37.4° (c = 1.0, CH_2Cl_2).

High Resolution MS (FAB, *m/z*): 359.2503 $(M+H)^+$, calculated for $C_{25}H_{31}N_2$ 359.2487.

1',3'-Dimethyl-4'*S*,5'*S*-diphenyl-2',3',3a*S*,6',7',7a'*R*-hexahydrospiro-[imidazolidine-2,1'(1*H*)-indene] (24).

The diene **23** (13.8 mg, 0.038 mmol) was dissolved in one drop of toluene-d_8 in a glass capillary and the capillary was then carefully sealed. The sealed capillary was submerged in a 145 °C oil bath for 20 d, after which time ^{1}H NMR showed the reaction to be complete with three products having been formed in a ratio 10 : 1.2 :1 (> 99% yield). Although these three products are not separable via column chromatography, it was possible to analyze the major one **24** by NMR.

Compound 24

^{1}H NMR (C_6D_6, 500 MHz) δ: 7.22-7.30 (10H, m), 6.02 (1H, dd, *J* = 9.5, 1.8 Hz), 5.76 (1H, ddd, *J* = 9.5, 3.2, 3.0 Hz), 3.93 (1H, d, *J* = 8.8 Hz), 3.68 (1H, d, *J* = 8.8 Hz), 2.60-2.62 (1H, m), 2.37 (3H, s), 2.24-2.36 (4H, m), 2.19 (3H, s), 2.02-2.04 (1H, m), 1.83-1.91 (3H, m), 1.36-1.44 (1H, m).

^{13}C NMR (toluene-d8, 126 MHz) δ: 140.87, 140.24, 131.67, 128.30, 128.02, 127.84, 127.64, 127.45, 127.18, 126.59, 89.01, 78.86, 75.57, 49.41, 40.46, 38.83, 32.69, 30.00, 26.59, 26.07, 25.18.

IR (CH_2Cl_2 film): 3086, 3013, 2937, 2843, 2791, 1653, 1585, 1495, 1452, 1294, 1174 cm^{-1}.

High Resolution MS (FAB, *m/z*): 357.2319 $(M-H)^+$, calculated for $C_{25}H_{29}N_2$ 357.2331.

1',3'-Dimethyl-4'*S*,5'*S*-diphenyl-2',3',3a*R*,4',5',6',7',7a'*R*-octahydrospiro[imidazolidine-2,1'(1*H*)-indene].

The Diels-Alder cycloadduct **24** (11.0 mg, 0.031 mmol) was dissolved in 4 mL 95% ethyl alcohol along with 4.8 mg 10% Pd/C (40 wt%). The mixture was stirred overnight at room temperature under a balloon filled with hydrogen gas. The solid was filtered, and the filtrate was concentrated *in vacuo*. Flash column chromatography (silica gel, hexane : Et_3N = 1 : trace) afforded the reduced product (9.2 mg, 87% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.14-7.27 (10H, m), 3.71 (1H, d, *J* = 8.8 Hz), 3.46 (1H, d, *J* = 8.8 Hz), 2.38 (3H, s), 2.24 (3H, s), 2.16-2.20 (1H, m), 1.96-1.99 (1H, m), 1.71-1.91 (6H, m), 1.48-1.53 (1H, m), 1.28-1.34 (3H, m), 1.96-1.99 (1H, m), 1.05-1.14 (1H, m).

^{13}C NMR ($CDCl_3$, 126 MHz) δ: 140.76, 140.17, 128.05, 127.98, 127.82, 127.69, 127.09, 126.87, 89.77, 78.15, 75.14, 52.36, 42.27, 38.29, 33.96, 32.89, 29.13, 28.46, 28.04, 26.36, 25.82.

IR (neat): 3086, 3028, 2928, 2849, 2791, 1603, 1495, 1452, 1271, 1163, 700 cm^{-1}.

$[\alpha]_D^{25}$ = -45.4° (c = 5.6, CH_2Cl_2).

High Resolution MS (FAB, *m/z*): 361.2644 $(M+H)^+$, calculated for $C_{25}H_{33}N_2$ 361.2643.

***Trans*-3a*R*,7a*S*-Octahydro-1*H*-inden-1-one (21A)**

The above aminal (9.2 mg, 0.026 mmol) was dissolved in 1 mL THF and 0.5 mL 1N HCl was added dropwise. After being stirred for 10 min, the reaction mixture was extracted with CH_2Cl_2 (3 x 1 mL) and the combined organic layers were dried over Na_2SO_4. Careful evaporation of the solvents gave an oily residue. Flash column chromatography (silica gel, pentane : ether = 10 : 1) afforded **26** (3.1 mg, 88% yield) as a colorless oil.

^1H NMR, especially ^{13}C NMR, data match the literature data.[2]

IR (neat): 2928, 2885, 1741, 1446, 1406 cm^{-1}.

$[\alpha]_D^{25} = +127.3^\circ$ (c = 0.55, CH_2Cl_2).

Circular Dichroism (CD): $\Delta\varepsilon = +0.80$ (cm_2mmol^{-1}), temperature (25 °C).

High Resolution MS (EI, *m/z*): 138.1043 (M^+), calculated for $C_9H_{14}O$ 138.1045.

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[2] Larock, R. C.; Oertle, K.; Potter, G. F. *J. Am. Chem. Soc.* **1980**, *102*,196.