Supporting Information

Total Synthesis of ($\pm$)-Lysergic Acid, Lysergol, and Isolysergol by Palladium-Catalyzed Domino Cyclization of Amino Allenes Bearing a Bromoindolyl Group

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Experimental Section

General Methods. All moisture-sensitive reaction were performed using syringe-septum cap techniques under an argon atmosphere and all glassware was dried in an oven at 80 °C for 2 h prior to use. Reactions at –78 °C employed a CO₂–MeOH bath. Melting points were measured by a hot stage melting point apparatus and are uncorrected. For flash chromatography, Wakosil C-300 was employed. ¹H NMR spectra were recording using a JEOR AL-400 or JEOL ECA-500 spectrometer, and chemical shifts are reported in δ (ppm) relative to TMS (in CDCl₃) as internal standard. ¹³C NMR spectra were recorded using a JEOR AL-400 or JEOL ECA-500 spectrometer and referenced to the residual CHCl₃ signal. NOE spectra were recorded on 500 MHz instruments. Chemical shifts were reported in parts per million with the residual solvent peak used as an internal standard. ¹H NMR spectra are tabulated as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), number of protons, and coupling constant(s). Exact mass (HRMS) spectra were recorded on a JMS-HX/HX 110A mass spectrometer. Infrared (IR) spectra were obtained on a JASCO FT/IR-4100 FT-IR spectrometer with JASCO ATR PRO410-S. Microwave reaction was conducted in a sealed glass vessel (capacity 10 mL) using CEM Discover microwave reactor. The temperature was monitored using IR sensor mounted under the reaction vessel. For analytical HPLC, a Cosmosil 5C18-ARII column (4.6 × 250 mm, Nacalai Tesque Inc., Kyoto, Japan) was employed on a Shimadzu LC-10ADvp (Shimadzu Corp., Ltd., Kyoto, Japan). Preparative HPLC was performed using a Cosmosil 5C18-ARII column (20 × 250 mm, Nacalai Tesque Inc.) on a Shimadzu LC-6AD (Shimadzu Corp., Ltd.).

4-Bromo-1-tosyl-1H-indole-3-carbaldehyde (S1). The formylation of 4-bromoindole was carried out according to the method of Shea.¹ To a stirred DMF (6 mL) was added POCl₃ (0.98 mL, 10.5 mmol) at 0 °C under argon. The solution was stirred for 2 min, and then 4-bromoindole (940 mg, 4.7 mmol) in DMF (5 mL) was added. The mixture was stirred for 1 h at room temperature and was slowly quenched with KOH (2.66 g) in water (10 mL). The reaction mixture was left to cool overnight, and was then partitioned between EtOAc and saturated aqueous NaHCO₃. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure to give off a crude aldehyde as a white solid. To a stirred solution of this aldehyde in CH₂Cl₂ (40 mL) were added TsCl (1.08 g, 5.6 mmol), Et₃N (1.05 mL, 7.5 mmol) and DMAP (57.4 mg, 0.47 mmol) at 0 °C, and the mixture was stirred for 2 h at room temperature. The mixture was made acidic with 1N HCl, and whole was extracted with EtOAc. The extract was washed with brine, dried over

MgSO₄, and concentrated under pressure to give a white solid, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (7:1) to give **S1** (1.59 g, 90% yield). Recrystallization from *n*-hexane–chloroform gave essentially pure **S1** as colorless crystals: mp 176 °C; IR (ATR): 1676 (C=O), 1381 (NSO₂), 1176 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 2.38 (s, 3H), 7.24 (dd, *J* = 8.2, 8.2 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 1H), 8.41 (s, 1H), 10.29 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.7, 112.9, 113.9, 122.0, 126.1, 127.0, 127.3 (2C), 128.9, 130.4 (2C), 132.0, 134.1, 136.2, 146.4, 186.2. *Anal.* Calcd for C₁₆H₁₂BrNO₃S: C, 50.81; H, 3.20; N, 3.70. Found: C, 50.81; H, 3.16; N, 3.71.

4-Bromo-3-(bromomethyl)-1-tosyl-1H-indole (9). To a stirred solution of the aldehyde **S1** (4.30 g, 11.4 mmol) in MeOH (300 mL) was added NaBH₄ (1.24 g, 32.7 mmol) at 0 °C. After stirring for 1.5 h at room temperature, H₂O was added, and the mixture was concentrated under reduced pressure. The residue was diluted with Et₂O, and the organic phase was separated and washed with brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a crude alcohol as a white solid, which was used without further purification. To a stirred solution of this alcohol in CH₂Cl₂ (60 mL) was added Ph₃PBr₂ (5.30 g, 12.5 mmol) in CH₂Cl₂ (50 mL). The mixture was stirred overnight at room temperature. Concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (7:1) to give **9** (4.46 g, 89% yield). Recrystallization from *n*-hexane–chloroform gave pure **9** as colorless crystals: mp 157 °C; IR (ATR): 1375 (NSO₂), 1173 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 2.36 (s, 3H), 4.88 (s, 2H), 7.17 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.75 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 24.7, 112.9, 114.2, 119.6, 126.1, 127.0 (2C), 127.1, 127.9, 128.2, 130.1 (2C), 134.7, 136.3, 145.6. *Anal.* Calcd for C₁₆H₁₃Br₂NO₂S: C, 43.36; H, 2.96; N, 3.16. Found: C, 43.57; H, 2.75; N, 2.90.

4-Bromo-1-tosyl-3-[2-(trimethylsilyl)ethynyl]-1,3-dithian-2-ylmethyl-1H-indole (11). To a stirred solution of the 2-(trimethylsilyl)ethynyl-1,3-dithiane **10** (38.3 mg, 0.177 mmol) in THF (1

mL) was added *n*-BuLi (1.65 M solution in hexane; 0.12 mL, 0.195 mmol) at $-40\text{ }^{\circ}\text{C}$ under argon. After stirring for 1 h with warming to $-20\text{ }^{\circ}\text{C}$, a solution of the bromide **9** (72.5 mg, 0.164 mmol) in THF (0.2 mL) was added to this reagent at $-20\text{ }^{\circ}\text{C}$. The mixture was stirred for 2 h at this temperature and quenched with H_2O . The whole was extract with Et_2O . The extract was washed with brine and dried over MgSO_4 . The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane– EtOAc (7:1) to give **11** (90.6 mg, 96% yield). Recrystallization from MeCN gave pure **11** as colorless crystals: mp $138\text{ }^{\circ}\text{C}$; IR (ATR): 2157 ($\text{C}\equiv\text{C}$), 1374 (NSO_2), 1173 (NSO_2); ^1H NMR (500 MHz, CDCl_3) δ 0.05 (s, 9H), 1.82–1.92 (m, 1H), 2.14–2.21 (m, 1H), 2.33 (s, 3H), 2.83 (ddd, $J = 13.9, 3.3, 3.3\text{ Hz}$, 2H), 3.29–3.37 (m, 2H), 3.78 (s, 2H), 7.07 (dd, $J = 8.0, 8.0\text{ Hz}$, 1H), 7.18 (d, $J = 8.2\text{ Hz}$, 2H), 7.36 (d, $J = 8.0\text{ Hz}$, 1H), 7.72 (d, $J = 8.2\text{ Hz}$, 2H), 7.91 (d, $J = 8.0\text{ Hz}$, 1H), 7.94 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 0.00 (3C), 21.8, 25.8, 29.1 (2C), 36.7, 47.1, 93.1, 103.2, 113.1, 115.0, 116.1, 125.3, 127.2 (2C), 128.4, 128.6, 129.5, 130.1 (2C), 135.2, 136.1, 145.2. *Anal.* Calcd for $\text{C}_{25}\text{H}_{28}\text{BrNO}_2\text{S}_3\text{Si}$: C, 51.89; H, 4.88; N, 2.42. Found: C, 51.66; H, 4.78; N, 2.24.

($\pm$)-1-(4-Bromo-1-tosyl-1H-indol-3-yl)-4-(trimethylsilyl)but-3-yn-2-ol (**S2**). To a stirred mixture of NCS (786 mg, 5.89 mmol) and AgNO_3 (1.03 g, 6.06 mmol) in MeCN (25 mL) and H_2O (5 mL) was added thioacetal **11** (1.00 g, 1.73 mmol) in MeCN (8 mL) at $0\text{ }^{\circ}\text{C}$. The mixture was stirred for 5 min at this temperature and quenched with saturated Na_2SO_3 , saturated NaHCO_3 and brine (1:1:1). The mixture was filtered through a short pad of celite with EtOAc . The filtrate was extract with Et_2O . The extract was washed with saturated Na_2SO_3 , saturated NaHCO_3 and brine (1:1:1), brine and dried over MgSO_4 . The filtrate was concentrated under reduced pressure to give a yellow oily residue, which was used without further purification. To a stirred solution of the crude ketone in MeOH (50 mL) was added $\text{CeCl}_3\cdot 7\text{H}_2\text{O}$ (838 mg, 2.25 mmol) at room temperature. After stirring for 10 min, NaBH_4 (118 mg, 3.11 mmol) was added to this solution at $-20\text{ }^{\circ}\text{C}$. The mixture was stirred for 1 h at this temperature and quenched with H_2O . The mixture was concentrated under reduced pressure. The residue was diluted with Et_2O , and the extract was washed with brine and dried over MgSO_4 . The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane– EtOAc (4:1) to give **S2** as a white amorphous (530 mg, 63% yield). IR (ATR): 3540 (OH), 2172 ($\text{C}\equiv\text{C}$), 1373 (NSO_2), 1173 (NSO_2); ^1H NMR (500 MHz, CDCl_3) δ 0.16 (s, 9H), 1.90 (d, $J = 5.1\text{ Hz}$, 1H), 2.35 (s, 3H), 3.33 (dd, $J = 14.0, 6.8\text{ Hz}$, 1H), 3.42 (dd, $J = 14.0, 6.8\text{ Hz}$, 1H), 4.72 (ddd, $J = 6.8, 6.8, 5.1\text{ Hz}$, 1H), 7.11 (dd, $J = 8.0, 8.0\text{ Hz}$, 1H), 7.23 (d, $J = 8.4\text{ Hz}$, 2H), 7.37 (d, $J = 8.0\text{ Hz}$, 1H), 7.59 (s, 1H), 7.73 (d, $J = 8.4$

Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 0.00 (3C), 21.8, 34.6, 63.1, 90.8, 105.9, 113.1, 114.6, 117.8, 125.5, 127.1 (2C), 127.2, 128.1, 128.9, 130.2 (2C), 135.2, 136.5, 145.4; HRMS (FAB) calcd $\text{C}_{22}\text{H}_{23}\text{BrNO}_3\text{SSi}$: $[\text{M} - \text{H}]^-$, 488.0357; found: $[\text{M} - \text{H}]^-$, 488.0351.

Methyl ($\pm$)-(E)-3-[1-(4-Bromo-1-tosyl-1H-indol-3-yl)but-3-yn-2-yloxy]acrylate (12**).** To a stirred solution of the alcohol **S2** (84.2 mg, 0.17 mmol) in THF (3 mL) was added TBAF (1.00 M solution in THF; 0.22 mL, 0.22 mmol) at 0 °C. The mixture was stirred for 1 h at this temperature and quenched with H_2O . The whole was extracted with EtOAc. The extract was washed with H_2O , brine and dried over MgSO_4 . The filtrate was concentrated under reduced pressure to give a pale yellow amorphous, which was used without further purification. To a stirred solution of this amorphous in Et_2O (1.5 mL) were added methyl propiolate (0.028 mL, 0.31 mmol) and Et_3N (0.043 mL, 0.31 mmol) at room temperature. The mixture was stirred overnight at room temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (4:1) to give **12** as a white amorphous (78.9 mg, 92% yield). IR (ATR): 2122 ($\text{C}\equiv\text{C}$), 1709 ($\text{C}=\text{O}$), 1625 ($\text{C}=\text{C}$), 1373 (NSO_2), 1173 (NSO_2); ^1H NMR (400 MHz, CDCl_3) δ 2.35 (s, 3H), 2.59 (d, $J = 2.1$ Hz, 1H), 3.47 (dd, $J = 13.9, 6.8$ Hz, 1H), 3.53 (dd, $J = 13.9, 6.8$ Hz, 1H), 3.70 (s, 3H), 4.90 (ddd, $J = 6.8, 6.8, 2.1$ Hz, 1H), 5.38 (d, $J = 12.4$ Hz, 1H), 7.14 (dd, $J = 8.0, 8.0$ Hz, 1H), 7.22 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 1H), 7.55 (s, 1H), 7.57 (d, $J = 12.4$ Hz, 1H), 7.71 (d, $J = 8.3$ Hz, 2H), 7.97 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 21.5, 32.2, 51.2, 71.0, 76.8, 79.6, 99.1, 113.1, 114.0, 116.2, 125.6, 126.8 (2C), 127.5, 127.9, 128.2, 130.0 (2C), 134.7, 136.4, 145.4, 159.9, 167.7; HRMS (FAB) calcd $\text{C}_{23}\text{H}_{19}\text{BrNO}_5\text{S}$: $[\text{M} - \text{H}]^-$, 500.0173; found: $[\text{M} - \text{H}]^-$, 500.0174.

($\pm$)-(E)-4-Bromo-1-tosyl-3-{2-[3-(triisopropylsilyloxy)prop-1-enyloxy]but-3-ynyl}-1H-indole (13**).** To a stirred solution of the enol ether **12** (200 mg, 0.40 mmol) in Et_2O (6.5 mL) was added DIBAL-H (0.99 M solution in toluene; 1.0 mL, 1.0 mmol) at -78 °C. The mixture was stirred for 50 min at this temperature and quenched with 2N Rochelle salt. After stirring for 1.5 h, the whole was extracted with Et_2O . The extract was washed with brine and dried over MgSO_4 . The filtrate was

concentrated under reduced pressure to give a crude alcohol as a white amorphous, which was used without further purification. To a stirred solution of this alcohol in DMF (2.0 mL) were added imidazole (81.7 mg, 1.2 mmol) and TIPSCl (0.127 mL, 0.60 mmol) at 0 °C. After stirring overnight at room temperature, the mixture was diluted with Et₂O. The organic phase was separated and washed with H₂O, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (15:1) to give **13** as a colorless oil (239 mg, 95% yield). IR (ATR): 2116 (C≡C), 1665 (C=C), 1369 (NSO₂), 1173 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 1.04–1.09 (m, 21H), 2.34 (s, 3H), 2.48 (d, *J* = 2.3 Hz, 1H), 3.37 (dd, *J* = 13.7, 6.9 Hz, 1H), 3.52 (dd, *J* = 13.7, 6.9 Hz, 1H), 4.19 (d, *J* = 6.3 Hz, 2H), 4.75 (ddd, *J* = 6.9, 6.9, 2.3 Hz, 1H), 5.19 (dt, *J* = 12.0, 6.3 Hz, 1H), 6.48 (d, *J* = 12.0 Hz, 1H), 7.11 (dd, *J* = 8.3, 8.3 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.57 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 12.1 (3C), 18.0 (6C), 21.6, 32.4, 61.0, 69.2, 75.3, 81.2, 107.2, 113.0, 114.2, 117.1, 125.4, 126.9 (2C), 127.3, 127.9, 128.6, 129.9 (2C), 134.9, 136.3, 145.2, 145.5; HRMS (FAB) calcd C₃₁H₃₉BrNO₄SSi: [M – H][–], 628.1558; found: [M – H][–], 628.1555.

(±)-(2*S*,*aR*)-6-(4-Bromo-1-tosyl-1*H*-indol-3-yl)-2-(triisopropylsilyloxymethyl)hexa-3,4-dien-1-ol (**14a**) and (±)-(2*R*,*aR*)-Isomer (**14b**).

Microwave conditions (Table 1, entry 2): A solution of the silyl enol ether **13** (31 mg, 0.049 mmol) in CHCl₃ was heated under microwave irradiation at 120 °C for 12 min, then 150 °C for 12 min. The mixture was diluted with MeOH (0.4 mL), NaBH₄ (2.2 mg, 0.059 mmol) was added at room temperature. The mixture was stirred for 1 h at room temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give **14** as a colorless oil (25.4 mg, 82% yield, **a:b** = *ca.* 33:67).

Au-Catalyzed conditions (Table 1, entry 3): To a stirred solution of the silyl enol ether **13** (50 mg, 0.079 mmol) in CH₂Cl₂ (0.25 mL) was added [(Ph₃PAu)₃O]BF₄ (4.3 mg, 0.004 mmol) at room temperature. After stirring for 7.5 h at 40 °C, the mixture was diluted with MeOH (0.5 mL). NaBH₄ (3.6 mg, 0.095 mmol) was added at room temperature, and the mixture was stirred for 1 h at room temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give **14** as a colorless oil (39.1 mg, 78% yield, **a:b** = *ca.* 80:20). Both diastereomers were isolated by HPLC [5C18-ARII column, 254 nm, MeCN:H₂O = 86:14, 8 mL/min; for analytical HPLC: 1 mL/min, *t*₁ = 48.25 min (minor isomer), *t*₂ = 49.80 min (major isomer)].

14a: IR (ATR): 3456 (OH), 1963 (C=C=C), 1374 (NSO₂), 1173 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 1.07-1.10 (m, 21H), 2.34 (s, 3H), 2.39-2.46 (m, 1H), 2.59 (dd, *J* = 6.3, 5.2 Hz, 1H), 3.52-3.72 (m, 5H), 3.78 (dd, *J* = 9.7, 4.6 Hz, 1H), 5.02 (ddd, *J* = 9.7, 6.3, 2.9 Hz, 1H), 5.45 (ddd, *J* = 13.1, 6.3, 2.3 Hz, 1H), 7.11 (dd, *J* = 8.5, 8.0 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.36 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.44 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.95 (dd, *J* = 8.5, 1.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 11.8 (3C), 17.9 (6C), 21.6, 26.5, 42.7, 65.9, 66.8, 89.8, 90.8, 112.9, 114.5, 121.8, 125.1, 125.4, 126.8 (2C), 127.7, 128.7, 129.9 (2C), 134.9, 136.5, 145.1, 204.7; HRMS (FAB) calcd C₃₁H₄₁BrNO₄SSi: [M – H][–], 630.1714; found: [M – H][–], 630.1707.

14b: IR (ATR): 3441 (OH), 1963 (C=C=C), 1375 (NSO₂), 1173 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 1.02-1.07 (m, 21H), 2.35 (s, 3H), 2.38-2.46 (m, 1H), 2.60-2.67 (m, 1H), 3.55-3.72 (m, 5H), 3.78 (dd, *J* = 9.7, 4.0 Hz, 1H), 5.06 (ddd, *J* = 9.7, 6.3, 2.9 Hz, 1H), 5.44 (ddd, *J* = 13.2, 6.3, 2.3 Hz, 1H), 7.11 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 11.8 (3C), 17.9 (6C), 21.6, 26.5, 42.6, 66.0, 66.9, 89.8, 90.9, 112.9, 114.5, 121.8, 125.1, 125.4, 126.8 (2C), 127.7, 128.7, 129.9 (2C), 135.0, 136.5, 145.2, 204.7; HRMS (FAB) calcd C₃₁H₄₁BrNO₄SSi: [M – H][–], 630.1714; found: [M – H][–], 630.1705.

Determination of Relative Configuration of **14a**:^{2,3}

(±)-4-Bromo-1-tosyl-3-[(2*R*,5*S*)-5-(triisopropylsilyloxymethyl)-5,6-dihydro-2*H*-pyran-2-yl]methyl-1*H*-indole (S3**)**. To a stirred suspension of AgBF₄ (3.1 mg, 0.016 mmol) in toluene (2.5 mL) was added Ph₃PAuCl (7.8 mg, 0.016 mmol) at room temperature. After stirring rapidly for 5 min, the resulting mixture was filtered through a cotton plug. To a solution of allenol **14a** (20 mg, 0.032 mmol) in toluene (0.25 mL) was added the above filtrate (0.25 mL) at room temperature. The

resulting mixture was stirred for 8.5 h at this temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (15:1) to give **S3** as a colorless oil (12.5 mg, 63% yield).

IR (ATR): 1598 (C=C), 1375 (NSO₂), 1173 (NSO₂); ¹H NMR (500 MHz, C₆D₆) δ 1.11–1.18 (m, 21H), 1.64 (s, 3H), 2.09–2.16 (br m, 1H), 3.16 (d, *J* = 6.3 Hz, 2H), 3.56 (dd, *J* = 11.2, 3.7 Hz, 1H), 3.72 (dd, *J* = 9.2, 5.4 Hz, 1H), 3.82 (dd, *J* = 9.2, 9.2 Hz, 1H), 4.15 (d, *J* = 11.2 Hz, 1H), 4.37–4.42 (m, 1H), 5.64 (d, *J* = 10.6 Hz, 1H), 5.70 (dd, *J* = 10.6, 4.3 Hz, 1H), 6.50 (d, *J* = 8.6 Hz, 2H), 6.71 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.72 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 12.0 (3C), 18.1 (6C), 21.6, 32.1, 38.3, 64.4, 73.5, 77.2, 113.0, 114.5, 119.4, 125.2, 126.4, 126.6, 126.9 (2C), 127.9, 129.0, 129.9 (2C), 131.0, 135.0, 136.5, 145.1; HRMS (FAB) calcd C₃₁H₄₁BrNO₄SSi: [M + H]⁺, 630.1714; found: [M + H]⁺, 630.1711.

Selected NOE cross peaks for pyran **S3**

***N*-[*(2S,aR)*-6-(4-Bromo-1-tosyl-1*H*-indol-3-yl)-2-(triisopropylsilyloxymethyl)hexa-3,4-dienyl]-2-nitrobenzenesulfonamide (**15a**) and Its (*±*)-(*2R,aR*)-Isomer (**15b**)**. To a stirred mixture of the allenol **14** (*a:b* = *ca.* 80:20) (300 mg, 0.48 mmol), NsNH₂ (317 mg, 1.57 mmol) and PPh₃ (630 mg, 2.40 mmol) in benzene (18 mL) was added diethyl azodicarboxylate (40% solution in toluene; 1.10 mL, 2.40 mmol) at room temperature, and the mixture was stirred for 1.5 h at this temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (3:1) to give **15** as a pale yellow amorphous (276 mg, 70% yield, *a:b* = 80:20).

15a (major): IR (ATR): 1962 (C=C=C), 1540 (NO₂), 1372 (NSO₂), 1172 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.99-1.07 (m, 21H), 2.35 (s, 3H), 2.36-2.42 (m, 1H), 3.05 (ddd, *J* = 12.6, 6.3, 5.1 Hz, 1H), 3.27 (ddd, *J* = 12.6, 6.3, 5.3 Hz, 1H), 3.39 (dd, *J* = 10.3, 8.0 Hz, 1H), 3.56-3.70 (m, 2H), 3.61 (dd, *J* = 10.3, 4.6 Hz, 1H), 5.04 (ddd, *J* = 9.7, 6.3, 2.9 Hz, 1H), 5.49 (ddd, *J* = 13.2, 6.3, 2.3 Hz, 1H), 5.67 (t, *J* = 6.3 Hz, 1H), 7.10 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.64-7.70 (m, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.79 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.09 (dd, *J* = 7.2, 2.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 11.8 (3C), 18.0 (6C), 21.6, 26.5, 41.5, 45.2, 65.1, 90.1, 91.8, 112.9, 114.4, 121.7, 125.0, 125.2, 125.5, 126.8 (2C), 127.7, 128.6, 130.0 (2C), 131.0, 132.6, 133.4, 133.8, 134.9, 136.5, 145.3, 148.0, 204.5; HRMS (FAB) calcd C₃₇H₄₅BrN₃O₇S₂Si: [M – H][–], 814.1657; found: [M – H][–], 814.1662.

15b (minor): IR (ATR): 1963 (C=C=C), 1541 (NO₂), 1372 (NSO₂), 1172 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.99-1.05 (m, 21H), 2.31-2.34 (m, 1H), 2.35 (s, 3H), 3.10 (ddd, *J* = 12.6, 6.3, 5.7 Hz, 1H), 3.30 (ddd, *J* = 12.6, 6.3, 6.3 Hz, 1H), 3.40 (dd, *J* = 9.7, 7.4 Hz, 1H), 3.61 (dd, *J* = 9.7, 4.9 Hz, 1H), 3.61-3.64 (m, 2H), 5.00 (ddd, *J* = 9.7, 6.9, 3.4 Hz, 1H), 5.41 (ddd, *J* = 13.2, 6.9, 1.7 Hz, 1H), 5.65 (t, *J* = 6.3 Hz, 1H), 7.10 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.61-7.69 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.77 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.09 (dd, *J* = 7.4, 1.7 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 11.8 (3C), 18.0 (6C), 21.6, 26.4, 41.6, 45.5, 65.1, 90.0, 91.5, 112.9, 114.5, 121.6, 125.1, 125.2, 125.4, 126.8 (2C), 127.7, 128.7, 130.0 (2C), 131.0, 132.6, 133.3, 133.8, 134.9, 136.5, 145.3, 148.0, 204.8; HRMS (FAB) calcd C₃₇H₄₅BrN₃O₇S₂Si: [M – H][–], 814.1657; found: [M – H][–], 814.1655.

(±)-*N*-[(2*S*,*aR*)-6-(4-bromo-1-tosyl-1*H*-indol-3-yl)-2-(triisopropylsilyloxymethyl)hexa-3,4-dienyl]-4-methylbenzenesulfonamide (**16a**) and Its (±)-(*2R*,*aR*)-Isomer (**16b**). To a stirred mixture of the allenol **14** (**a**:**b** = *ca.* 80:20; 150 mg, 0.24 mmol), FmocNHTs (308 mg, 0.78 mmol) and PPh₃ (312 mg, 1.19 mmol) in THF (4 mL) was added diethyl azodicarboxylate (0.54 mL, 1.19 mmol; 40% solution in toluene) at 0 °C, and the mixture was stirred for 3 h at room temperature. Concentration under pressure gave an oily residue, which was dissolved in DMF (7 mL). Piperidine (94 μL, 0.95 mmol) was added to the mixture at 0 °C. After stirring for 50 min at room temperature,

the mixture was diluted with Et₂O and washed with H₂O, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **16** as a yellow amorphous (136 mg, 73% yield, **a:b** = *ca.* 80:20).

16a (major): IR (ATR): 1964 (C=C=C), 1374 (NSO₂), 1173 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.98-1.04 (m, 21H), 2.29-2.34 (m, 1H), 2.34 (s, 3H), 2.40 (s, 3H), 2.98 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.00 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.36 (dd, *J* = 10.0, 8.3 Hz, 1H), 3.60 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.60-3.64 (m, 2H), 4.96 (ddd, *J* = 9.1, 6.3, 2.9 Hz, 1H), 5.14 (t, *J* = 6.0 Hz, 1H), 5.44 (ddd, *J* = 13.2, 6.3, 2.3 Hz, 1H), 7.10 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.41 (s, 1H), 7.70-7.74 (m, 4H), 7.94 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 11.7 (3C), 17.9 (6C), 21.5, 21.6, 26.4, 40.5, 45.9, 66.4, 90.2, 91.6, 112.9, 114.4, 121.6, 125.1, 125.5, 126.8 (2C), 127.1 (2C), 127.7, 128.6, 129.6 (2C), 130.0 (2C), 134.9, 136.5, 137.0, 143.2, 145.2, 204.5; HRMS (FAB) calcd C₃₈H₄₈BrN₂O₅S₂Si: [M – H][–], 783.1963; found: [M – H][–], 783.1960.

16b (minor): IR (ATR): 1964 (C=C=C), 1374 (NSO₂), 1173 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.94-1.04 (m, 21H), 2.27-2.33 (m, 1H), 2.35 (s, 3H), 2.41 (s, 3H), 2.99 (ddd, *J* = 6.3, 6.3, 1.7 Hz, 1H), 3.01 (ddd, *J* = 6.3, 6.3, 1.7 Hz, 1H), 3.35 (dd, *J* = 10.0, 7.7 Hz, 1H), 3.60 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.61-3.65 (m, 2H), 4.94 (ddd, *J* = 9.7, 6.3, 2.9 Hz, 1H), 5.11 (t, *J* = 6.3 Hz, 1H), 5.42 (ddd, *J* = 13.2, 6.3, 2.3 Hz, 1H), 7.10 (dd, *J* = 8.2, 8.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.41 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 11.7 (3C), 17.9 (6C), 21.5, 21.6, 26.3, 40.5, 46.0, 66.4, 90.2, 91.5, 112.9, 114.4, 121.5, 125.1, 125.4, 126.8 (2C), 127.1 (2C), 127.7, 128.6, 129.6 (2C), 130.0 (2C), 134.9, 136.5, 137.0, 143.2, 145.2, 204.6; HRMS (FAB) calcd C₃₈H₄₈BrN₂O₅S₂Si: [M – H][–], 783.1963; found: [M – H][–], 783.1968.

(±)-(6aR,9S)-7-(2-Nitrophenylsulfonyl)-4-tosyl-9-(triisopropylsilyloxymethyl)-4,6,6a,7,8,9-hexahydroindolo[4,3-fg]quinoline (**17a**) and Its (±)-(6aS,9S)-Isomer (**17b**). To a stirred mixture of allenamide **15** (**a:b** = 80:20; 30 mg, 0.037 mmol) in DMF (0.6 mL) were added Pd(PPh₃)₄ (2.1 mg, 0.0018 mmol) and K₂CO₃ (15 mg, 0.11 mmol) at room temperature under argon, and the mixture was stirred for 3.5 h at 100 °C. The mixture was dilute with Et₂O and washed with H₂O, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a yellow oil which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give **17** as a yellow amorphous (22.3 mg, 83% yield, **a:b** = 73:27). Both diastereomers were isolated by PTLC with hexane–*i*-Pr₂O (3:1).

17a (major): IR (ATR): 1596 (C=C), 1544 (NO₂), 1359 (NSO₂), 1178 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.97-1.04 (m, 21H), 2.36 (s, 3H), 2.40-2.48 (br m, 1H), 2.95 (dd, *J* = 13.7, 10.9 Hz, 1H), 2.99 (ddd, *J* = 14.9, 12.0, 2.3 Hz, 1H), 3.27 (dd, *J* = 14.9, 5.2 Hz, 1H), 3.55 (dd, *J* = 9.7, 8.0 Hz, 1H), 3.69 (dd, *J* = 9.7, 5.7 Hz, 1H), 4.10 (dd, *J* = 13.7, 5.2 Hz, 1H), 4.75-4.80 (m, 1H), 6.16 (s, 1H), 7.18-7.21 (m, 2H), 7.23-7.30 (m, 3H), 7.60-7.65 (m, 2H), 7.66-7.71 (m, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 7.4 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 11.8 (3C), 17.9 (6C), 21.6, 29.7, 38.2, 43.0, 54.1, 64.9, 112.7, 115.6, 117.3, 120.5, 124.0, 124.3, 125.8, 126.8 (2C), 128.2, 130.0 (2C), 130.2, 131.0, 131.8, 133.4, 133.5, 133.6, 133.8, 135.4, 144.9, 147.9; HRMS (FAB) calcd C₃₇H₄₄N₃O₇S₂Si: [M – H][–], 734.2395; found: [M – H][–], 734.2392.

17b (minor): IR (ATR): 1597 (C=C), 1542 (NO₂), 1359 (NSO₂), 1174 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.94-1.01 (m, 21H), 2.36 (s, 3H), 2.53-2.58 (br m, 1H), 2.99 (ddd, *J* = 14.3, 12.0, 2.3 Hz, 1H), 3.12 (dd, *J* = 14.3, 5.0 Hz, 1H), 3.33 (dd, *J* = 9.7, 8.0 Hz, 1H), 3.35 (dd, *J* = 13.7, 3.4 Hz, 1H), 3.48 (dd, *J* = 9.7, 6.9 Hz, 1H), 3.97 (d, *J* = 13.7 Hz, 1H), 4.74 (dd, *J* = 12.0, 5.0 Hz, 1H), 6.31 (d, *J* = 5.2 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.18 (d, *J* = 6.9 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.28 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.62-7.72 (m, 3H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 8.14 (dd, *J* = 7.4, 1.7 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 11.9 (3C), 18.0 (6C), 21.6, 28.7, 39.5, 40.3, 53.9, 63.9, 112.7, 115.7, 117.2, 120.4, 123.1, 124.3, 125.8, 126.8 (2C), 128.2, 130.0 (2C), 130.6, 131.4, 131.9, 133.3, 133.6, 134.0, 134.1, 135.4, 144.9, 147.8; HRMS (FAB) calcd C₃₇H₄₄N₃O₇S₂Si: [M – H][–], 734.2395; found: [M – H][–], 734.2392.

(±)-(6a*R*,9*S*)-4,7-Ditosyl-9-(triisopropylsilyloxymethyl)-4,6,6a,7,8,9-hexahydroindolo[4,3-fg]quinoline (**18a**) and Its (±)-(6a*S*,9*S*)-Isomer (**18b**). To a stirred mixture of allenamide **16** (**a:b** = *ca.* 80:20; 30 mg, 0.038 mmol) in DMF (0.6 mL) were added Pd(PPh₃)₄ (2.2 mg, 0.0019 mmol) and K₂CO₃ (15.8 mg, 0.11 mmol) at room temperature under argon, and the mixture was stirred for 3 h at 120 °C. The mixture was diluted with Et₂O and washed with H₂O, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a yellow oil which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (6:1) to give **18** as a white amorphous (17.3 mg, 65% yield, **a:b** = 87:13). Both diastereomers were isolated by PTLC with hexane–*i*-Pr₂O (1:1).

18a (major): IR (ATR): 1598 (C=C), 1376 (NSO₂), 1178 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.95-1.05 (m, 21H), 2.12-2.19 (br m, 1H), 2.35 (s, 3H), 2.39 (s, 3H), 2.84 (dd, *J* = 13.7, 10.6 Hz, 1H), 2.92 (ddd, *J* = 14.0, 12.0, 1.7 Hz, 1H), 3.33 (dd, *J* = 14.0, 5.4 Hz, 1H), 3.46 (dd, *J* = 9.6, 8.6 Hz, 1H), 3.63 (dd, *J* = 9.6, 5.4 Hz, 1H), 4.11 (dd, *J* = 13.7, 5.2 Hz, 1H), 4.67-4.73 (m, 1H), 6.07 (s, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.20-7.28 (m, 6H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 7.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 11.9 (3C), 17.9 (6C), 21.5, 21.6, 30.0, 37.3, 42.9, 53.6, 65.0, 112.7, 115.5, 117.7, 120.5, 124.0, 125.7, 126.8 (2C), 126.9 (2C), 128.3, 129.8 (2C), 129.9 (2C), 130.2, 133.3, 133.4, 135.5, 138.0, 143.3, 144.8; HRMS (FAB) calcd C₃₈H₄₉N₂O₅S₂Si: [M + H]⁺, 705.2852; found: [M + H]⁺, 705.2850.

18b (minor): IR (ATR): 1598 (C=C), 1377 (NSO₂), 1173 (NSO₂), ¹H NMR (500 MHz, CDCl₃) δ 0.99-1.05 (m, 21H), 2.35 (s, 3H), 2.40 (s, 3H), 2.49-2.55 (br m, 1H), 2.87 (ddd, *J* = 14.3, 12.0, 1.7 Hz, 1H), 3.21 (dd, *J* = 13.2, 3.7 Hz, 1H), 3.30-3.39 (m, 3H), 3.89 (d, *J* = 13.2 Hz, 1H), 4.64 (dd, *J* = 11.5, 4.6 Hz, 1H), 6.29 (d, *J* = 5.2 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.18 (s, 1H), 7.22-7.29 (m, 5H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 11.9 (3C), 18.0 (6C), 21.5, 21.6, 28.4, 39.5, 39.9, 53.7, 64.3, 112.7, 115.6, 117.6, 120.5, 123.6, 125.8, 126.8 (2C), 127.1 (2C), 128.3, 129.7 (2C), 129.9 (2C), 130.7, 133.3, 134.1, 135.5, 138.1, 143.2, 144.8; HRMS (FAB) calcd C₃₈H₄₉N₂O₅S₂Si: [M + H]⁺, 705.2852; found: [M + H]⁺, 705.2849.

Determination of Relative Configuration of 18a:

To a stirred mixture of **17a** (25 mg, 0.034 mmol) in DMF (0.2 mL) were added LiOH·H₂O (14.3 mg 0.34 mmol) and HSCH₂CO₂H (11.8 μL, 0.17 mmol) at 0 °C. After stirring for 1 h at room temperature, the mixture was diluted with EtOAc was washed with saturated NaHCO₃, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a crude amine as an oily residue, which was used without further purification. To a stirred solution of this amine in CH₂Cl₂ (0.25 mL) were added Et₃N (14.2 μL, 0.102 mmol) and TsCl (9.7 mg, 0.051 mmol) at 0 °C. After stirring for 2 h at room temperature, the mixture was diluted with EtOAc and washed with H₂O, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (6:1) to give **18a** as a white amorphous (18.1 mg, 76% yield).

Determination of Relative Configuration of 18b:

By a procedure identical with that described for synthesis of **18a** from **17a**, the nosylamide **17b** (24 mg, 0.033 mmol) was converted into **18b** as a white amorphous (13.8 mg, 59% yield).

(±)-(6a*R*,9*S*)-7-Methyl-4-tosyl-9-(triisopropylsilyloxymethyl)-4,6,6a,7,8,9-hexahydroindolo[4,3-fg]quinoline (**S4a**) and Its (±)-(6a*S*,9*S*)-Isomer (**S4b**). To a stirred mixture of **17** (a:b = 74:26) (136 mg, 0.19 mmol) in DMF (1.1 mL) were added LiOH·H₂O (78 mg 1.9 mmol) and HSCH₂CO₂H (64 μL, 0.92 mmol) at 0 °C. After stirring for 1 h at room temperature, the mixture was diluted with

EtOAc and washed with saturated NaHCO₃, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a crude amine as an oily residue, which was used without further purification. To a stirred solution of this amine in DMF (2.0 mL) were added K₂CO₃ (41 mg, 0.30 mmol) and MeI (15 μ L, 0.24 mmol) at 0 °C. After stirring for 5 h at room temperature, the mixture was diluted with EtOAc and washed with saturated NaHCO₃, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (5:1 to 3:1) to give **S4a** (53.4 mg, 52% yield) and **S4b** (16.7 mg, 16% yield) both as a brown amorphous.

S4a: IR (ATR): 1599 (C=C), 1379 (NSO₂), 1177 (NSO₂), ¹H NMR (500 MHz, CDCl₃) δ 1.03-1.09 (m, 21H), 2.33 (s, 3H), 2.46 (s, 3H), 2.48-2.53 (m, 3H), 2.95-3.04 (m, 2H), 3.37 (dd, *J* = 15.4, 5.4 Hz, 1H), 3.72 (dd, *J* = 9.3, 5.2 Hz, 1H), 3.78 (dd, *J* = 9.3, 9.0 Hz, 1H), 6.37 (d, *J* = 3.9 Hz, 1H), 7.16-7.21 (m, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.23-7.29 (m, 2H), 7.72-7.76 (m, 1H), 7.74 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 12.0 (3C), 18.0 (6C), 21.5, 27.2, 39.2, 43.7, 53.0, 62.2, 65.0, 112.2, 116.1, 118.4, 119.7, 123.2, 125.8, 126.7 (2C), 128.6, 129.8 (2C), 129.9, 133.5, 135.0, 135.5, 144.6; HRMS (FAB) calcd C₃₂H₄₃N₂O₃SSi: [M – H][–], 563.2769; found: [M – H][–], 563.2770.

S4b: IR (ATR): 1599 (C=C), 1379 (NSO₂), 1178 (NSO₂), ¹H NMR (500 MHz, CDCl₃) δ 1.05-1.09 (m, 21H), 2.22 (dd, *J* = 10.7, 10.7 Hz, 1H), 2.33 (s, 3H), 2.50-2.58 (m, 4H), 2.82-2.93 (m, 1H), 2.98-3.01 (m, 1H), 3.07 (dd, *J* = 11.1, 5.0 Hz, 1H), 3.43 (dd, *J* = 15.1, 5.4 Hz, 1H), 3.65 (dd, *J* = 9.5, 7.6 Hz, 1H), 3.71 (dd, *J* = 9.5, 6.3 Hz, 1H), 6.38 (s, 1H), 7.19 (s, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.24-7.30 (m, 2H), 7.73-7.77 (m, 1H), 7.76 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 12.0 (3C), 18.0 (6C), 21.5, 27.0, 39.4, 44.0, 56.8, 62.5, 65.7, 112.2, 116.3, 118.1, 119.7, 123.9, 125.8, 126.7 (2C), 128.5, 129.6, 129.8, 133.5 (2C), 133.8, 135.6, 144.6; HRMS (FAB) calcd C₃₂H₄₃N₂O₃SSi: [M – H][–], 563.2769; found: [M – H][–], 563.2770.

(±)-Isolysergol (3). To a stirred solution of **S4a** (8.3 mg, 0.015 mmol) in THF (0.33 mL) was added TBAF (1.00 M solution in THF; 18 μ L, 0.018 mmol) at 0 °C. The mixture was stirred for 1 h at room temperature and quenched with H₂O. The whole was extract with EtOAc. The extract was washed with H₂O, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a crude alcohol as a brown amorphous, which was used without further purification. To a stirred solution of this alcohol in MeOH (0.45 mL) was added Mg (3.6 mg, 0.15 mmol) at room temperature. The mixture was stirred for 2 h at this temperature. Concentration under pressure

gave an oily residue, which was purified by PTLC with EtOAc–MeOH (3:1) to give isolysergol **3** as a pale brown solid (3.8 mg, 99% yield).

IR (ATR): 3213 (OH), 1604 (C=C), The IR spectra was found to be identical with that of natural isolysergol.⁴ ¹H NMR (500 MHz, CDCl₃–CD₃OD) δ 2.44–2.50 (m, 1H), 2.55 (s, 3H), 2.65 (ddd, J = 14.3, 11.5, 1.7 Hz, 1H), 2.85 (ddd, J = 11.5, 4.0, 1.7 Hz, 1H), 3.04 (d, J = 11.5 Hz, 1H), 3.14–3.19 (m, 1H), 3.53 (dd, J = 14.3, 5.7 Hz, 1H), 3.80 (ddd, J = 10.3, 3.6, 1.7 Hz, 1H), 3.96 (dd, J = 10.3, 3.4 Hz, 1H), 6.46 (d, J = 5.7 Hz, 1H), 6.89 (d, J = 1.7 Hz, 1H), 7.14–7.17 (m, 2H), 7.18–7.22 (m, 1H); The ¹H NMR spectra was found to be identical with that of synthesized isolysergol reported by Ninomiya and Naito.⁵ ¹³C NMR (125 MHz, CDCl₃–CD₃OD) δ 27.3, 36.3, 43.3, 57.4, 63.0, 66.0, 109.5, 109.9, 111.7, 118.2, 121.0, 122.9, 126.0, 128.0, 133.8, 136.7; HRMS (FAB) calcd C₁₆H₁₇N₂O: [M – H][–], 253.1346; found: [M – H][–], 253.1352.

(±)-Lysergol (2). To a stirred solution of **S4b** (16.7 mg, 0.030 mmol) in THF (0.7 mL) was added TBAF (1.00 M solution in THF; 39 μ L, 0.039 mmol) at 0 °C. The mixture was stirred for 1.5 h at room temperature and quenched with H₂O. The whole was extracted with EtOAc. The extract was washed with H₂O, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a crude alcohol as a brown amorphous, which was used without further purification. To a stirred solution of this alcohol in MeOH (0.85 mL) was added Mg (7.3 mg, 0.30 mmol) at room temperature. The mixture was stirred for 3 h at this temperature. Concentration under pressure gave an oily residue, which was purified by PTLC with ethyl acetate–MeOH (2:1) to give lysergol **2** as a pale brown solid (7.0 mg, 92% yield).

IR (ATR): 3427 (OH), 1606 (C=C), ^1H NMR (500 MHz, $\text{CDCl}_3\text{--CD}_3\text{OD}$) δ 2.36 (dd, $J = 10.9, 10.9$ Hz, 1H), 2.61 (s, 3H), 2.74 (ddd, $J = 13.7, 12.0, 1.7$ Hz, 1H), 2.85-2.93 (m, 1H), 3.17 (dd, $J = 10.9, 5.2$ Hz, 1H), 3.23-3.30 (m, 1H), 3.51-3.59 (m, 2H), 3.70 (dd, $J = 10.9, 5.7$ Hz, 1H), 6.41 (s, 1H), 6.94 (s, 1H), 7.13-7.18 (m, 2H), 7.20-7.25 (m, 1H); ^{13}C NMR (125 MHz, $\text{CDCl}_3\text{--CD}_3\text{OD}$) δ 26.3, 38.1, 43.2, 56.5, 63.1, 64.6, 109.5 (2C), 111.6, 118.4, 121.0, 122.8, 125.8, 127.6, 133.9, 135.0; The IR, ^1H NMR and ^{13}C NMR spectra were found to be identical with those of natural lysergol. HRMS (FAB) calcd $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}$: $[\text{M} - \text{H}]^-$, 253.1346; found: $[\text{M} - \text{H}]^-$, 253.1349.

19a

S16

Determination of Relative Configuration of 18b:

To a stirred solution of **19a** (5.0 mg, 0.0086 mmol) in MeOH (0.5 mL) was added NaBH₄ (1.63 mg, 0.043 mmol) at room temperature.⁶ After stirring for 1 h at this temperature, H₂O was added, and the mixture was concentrated under reduced pressure. The residue was dissolved in EtOAc and washed with brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a crude alcohol, which was used without further purification. To a stirred solution of this alcohol in DMF (0.2 mL) were added imidazole (16.6 mg, 0.24 mmol) and TIPSCl (0.026 mL, 0.12 mmol) at 0 °C. After stirring overnight at room temperature, the mixture was diluted with Et₂O and washed with H₂O, brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by PTLC with *n*-hexane–EtOAc (3:1) to give **18a** as a white amorphous (4.1 mg, 68% yield).

(±)-Methyl Isolysergate (20b) and (±)-Methyl Lysergate (20a). To a stirred solution of **19a** (30 mg, 0.052 mmol) in THF (1.6 mL) was added sodium naphthalenide (0.67 M solution in THF; 0.78 mL, 0.52 mmol)⁷ at –78 °C under argon. The mixture was stirred for 10 min at this temperature and quenched with saturated NH₄Cl. The mixture was made basic with saturated NaHCO₃. The whole was extracted with EtOAc. The extract was washed with brine and dried over MgSO₄. Concentration of the filtrate under reduced pressure gave a crude amine which was used without further purification. To a stirred solution of this amine in MeOH (3.0 mL) were added formalin (0.02 mL, 0.26 mmol), NaBH₃CN (16.3 mg, 0.26 mmol) and AcOH (55 μL) at room temperature. After stirring for 1.5 h at this temperature, the mixture was quenched with saturated NaHCO₃. The mixture was concentrated under pressure followed by filtration through a short pad of SiO₂ with EtOAc. The filtrate was concentrated under reduced pressure to give a yellow solid, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (1:10) to give **20a** and **20b** as a yellow solid (9.0 mg, 61% yield, **a:b** = 35:65).

¹H NMR spectra of **20a** and **20b** were in agreement with those reported by Hendrickson⁸: ¹H NMR

(400 MHz, CDCl₃) of methyl lysergate **20b** (minor isomer): δ 2.63 (s, 3H), 2.68-2.73 (m, 2H), 3.20-3.27 (m, 1H), 3.30 (dd, J = 11.6, 4.9 Hz, 1H), 3.53 (dd, J = 14.5, 5.5 Hz, 1H), 3.73-3.76 (m, 1H), 3.79 (s, 3H), 6.60 (s, 1H), 6.91 (t, J = 1.8 Hz, 1H), 7.16-7.25 (m, 3H), 7.92 (br s, 1H); methyl isolysergate **20a** (major isomer): δ 2.59 (s, 3H), 2.75-2.81 (m, 2H), 3.20-3.27 (m, 1H), 3.29-3.34 (m, 1H), 3.38 (dd, J = 11.6, 3.0 Hz, 1H), 3.44 (dd, J = 14.6, 5.4 Hz, 1H), 3.73 (s, 3H), 6.56 (d, J = 5.4 Hz, 1H), 6.91 (t, J = 1.8 Hz, 1H), 7.16-7.25 (m, 3H), 7.92 (br s, 1H); IR (ATR): 3410 (NH), 1731 (C=O), 1604 (C=C); HRMS (FAB) calcd C₁₇H₁₇N₂O₂: [M – H][–], 281.1296; found: [M – H][–], 281.1304.

(±)-Lysergic Acid (1). The preparation of lysergic acid (**1**) was carried out according to the method of Hendrickson⁸ and Szántay⁹: To solution of diastereomixture of methyl lysergate and isolysergate (20.6 mg, 0.073 mmol, **20a:b** = 35:65) in EtOH (0.68 mL) was added 1N NaOH (0.68 mL). The reaction mixture was stirred at 35 °C for 2 h. 0.1 N HCl solution was used to carefully adjust the pH to 6.2 and stirred for further 2 h at 0 °C while a solid material was formed. The precipitate was filtered off and washed with cold water and acetone to give **1** as a pale brown solid (10.6 mg, 54% yield). The IR, ¹H NMR and ¹³C NMR spectra were in agreement with those reported by Hendrickson⁸ and Szántay⁹: IR (ATR): 3240 (OH), 1589 (C=O), ¹H NMR (500 MHz, C₅D₅N) δ 2.53 (s, 3H), 2.88-2.96 (m, 2H), 3.27-3.33 (m, 1H), 3.53 (dd, J = 11.2, 5.4 Hz, 1H), 3.64 (dd, J = 14.6, 5.4 Hz, 1H), 4.03-4.08 (m, 1H), 7.20-7.26 (m, 2H), 7.30 (dd, J = 8.0, 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 11.68 (s, 1H); ¹H NMR (500 MHz, (CD₃)₂SO) δ 2.47 (s, 3H), 2.48-2.51 (m, 2H), 2.96-3.02 (m, 1H), 3.13 (dd, J = 11.5, 5.2 Hz, 1H), 3.46 (dd, J = 14.6, 5.4 Hz, 1H), 3.47-3.52 (m, 1H), 6.47 (br s, 1H), 7.01-7.08 (m, 3H), 7.18 (d, J = 7.4 Hz, 1H), 10.70 (br s, 1H); ¹³C NMR (125 MHz, C₅D₅N) δ 27.8, 43.2, 43.9, 56.0, 63.7, 110.4, 110.5, 112.2, 119.8, 120.1, 127.3, 128.8, 135.8, 136.7, 175.0 (one of the sp² carbons was overlapped with C₅D₅N solvent peaks); ¹³C NMR [125 MHz, (CD₃)₂SO] δ 26.6, 41.7, 43.2, 54.6, 62.5, 108.8, 109.9, 111.0, 118.7, 119.3, 122.3, 125.9, 127.3, 133.8, 135.4, 173.4; HRMS (FAB) calcd C₁₆H₁₇N₂O₂: [M – H][–], 269.1290; found: [M – H][–], 269.1289.

Reference:

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single_pulse

DFILE: 1016C-40-2-1.als
 COMNT: single_pulse
 DATIM: 20-06-2007 17:36:01
 OBNUC: ¹H
 EXMOD: single_pulse, ex2
 OBFRQ: 500.16 MHz
 OBSET: 2.41 KHz
 OBFIN: 6.01 Hz
 POINT: 52428
 FREQU: 7507.39 Hz
 SCANS: 8
 ACQTM: 6.9835 sec
 PD: 5.0000 sec
 PW1: 6.25 usec
 IRNUC: ¹H
 CTEMP: 25.0 c
 SLVNT: CDCl₃
 EXREF: 0.00 ppm
 BF: 1.20 Hz
 RGAIN: 44

1016C-40-2BCM

DFILE 1016C-40-2BCM1BCM_E16_FT.al
 COMNT 1016C-40-2BCM
 DATIM Wed Jun 20 16:33:50 2007
 OBNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 27118.64 Hz
 SCANS 512
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 5.10 usec
 IRNUC 1H
 CTEMP 23.7 c
 SLVNT CDCl3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

single_pulse

DFILE 1016C-43-1-1.als
 COMNT single_pulse
 DATIM 22-06-2007 10:13:12
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 52428
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 6.9835 sec
 PD 5.0000 sec
 PW1 6.25 usec
 IRNUC 1H
 CTEMP 25.2 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 1.20 Hz
 RGAIN 46

1016C-43BCM

DFILE 1016C-43BCM1BCM_E1_FT.als
 COMNT 1016C-43BCM
 DATIM Fri Jun 22 11:10:12 2007
 ORNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 27118.64 Hz
 SCANS 1024
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 5.10 usec
 IRNUC 1H
 CTEMP 23.7 c
 SLVNT CDCl3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

DFILE	1016C127_070915-2-2.als
COMNT	single_pulse
DATIM	15-09-2007 14:50:37
ORNUC	1H
EXMOD	single_pulse,ex2
OFBRQ	500.16 MHz
OBSET	2.41 kHz
OFBIN	6.01 Hz
POINT	52428
FREQU	7507.39 Hz
SCANS	8
ACQTM	6.9835 sec
PD	5.0000 sec
PW1	6.05 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	44

single pulse decoupled gated NOE

DFILE 1016C1278CM-1.als
 COMNT single pulse decoupled gate
 DATIM 15-09-2007 15:40:15
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 1024
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC 1H
 CTEMP 25.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 1.20 Hz
 RGAIN 58

single_pulse

DFILE 1016D4-1.als
 COMNT single_pulse
 DATIM 24-11-2007 11:39:40
 OBNUC ¹H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC ¹H
 CTMP 27.9 °C
 SLVNT CDCl₃
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 50

single pulse decoupled gated NMR

DF:FILE 1016C198BCM-date-1.als
 COMNT single pulse decoupled gate
 DATIM 21-11-2007 01:12:48
 OBNUC ¹³C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 1024
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC ¹H
 CTEMP 28.4 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 60

DFILE 1016D93a.als
 COMNT
 DATIM Wed Feb 20 22:24:20 2008
 OBNUC ¹H
 EXMOD NON
 OBFREQ 399.65 MHz
 OBFREQ 124.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 7992.01 Hz
 SCANS 8
 ACQTM 4.1001 sec
 PD 2.9000 sec
 5.50 usec
 PW1 ¹H
 IRNUC 27.1 °C
 CTEMP CDCL3
 SLVNT
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 23

single pulse decoupled gated NOF

DFILE 1016D93BCM-1.als
 COMNT single pulse decoupled gate
 DATIM 20-02-2008 23:12:49
 OBNUC ¹³C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 512
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC ¹H
 CTEMP 27.6 °C
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

single_pulse

DFILE 1016D105c-L.als
 COMNT single_pulse
 DATIM 26-02-2008 19:08:22
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTEMP 27.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 40

20.72

0.86

0.94

1.73

0.97

1.00

0.90

0.97

0.98

0.93

1.96

1.00

PPM

0

2

4

6

8

single pulse decoupled gated NOE

DFILE 10160105 BCM-1.als
 COMNT single pulse decoupled gate
 DATIM 26-02-2008 19:41:12
 OBNUC ¹³C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 500
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC ¹H
 CTEMP 27.7 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

single_pulse

DFILE: 1016010-major-b-l.als
 COMNT single_pulse
 DATIM 09-12-2007 21:05:27
 OBNUC 1H
 EXMOD single_pulse,ex2
 OBRFQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTEMP 25.8 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 36

21.44

single pulse decoupled gated NOE

DFILE 1016D10major-RCM-1.als
 COMNT single pulse decoupled gate
 DATIM 09-12-2007 21:31:34
 OBNUC ¹³C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 512
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC ¹H
 CTEMP 26.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 58

single_pulse

DFILE 1016010-miner-1.als
 COMNT single_pulse
 DATIM 09-12-2007 20:54:03
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTEMP 25.8 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 38

21.40

204.69

90.91
89.78
77.26
77.00
76.75
66.88
65.96
42.58
11.77

42.58
65.96
66.88
76.75
77.00
77.26
89.78
90.91

145.15
136.51
134.95
129.93
128.70
127.71
126.84
125.43
125.11
121.77
114.47
112.87

(±)-14b

single_pulse

DFILE 1016D68 benzene-d-1.als
 COMNT single_pulse
 DATIM 19-01-2008 17:58:41
 OBNUC 1H
 EXMOD single_pulse,ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTEMP 25.7 c
 SLVNT C6D6
 EXREF 0.00 ppm
 BF 0.10 Hz
 RGAIN 40

1016D28-1BCM

DFILE 1016D28-1BCM1BCM_E5_FT.a1s
 COMNT 1016D28-1BCM
 DATIM Thu Dec 20 03:28:29 2007
 ORNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 27118.64 Hz
 SCANS 2048
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 5.10 usec
 TRNUC 1H
 CTEMP 24.4 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 1.20 Hz
 RGAIN 26

single_pulse

DFILE 1016018major-a-l.als
 COMNT single_pulse
 DATIM 14-12-2007 21:06:33
 OBNUC 1H
 EXMOD single_pulse,ex2
 OBRFQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTEMP 26.7 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 38

single pulse decoupled gated NOE

DFILE 1016018major BCM-1.als
 COMNT single pulse decoupled gate
 DATIM 13-12-2007 22:17:26
 OBNUC ¹³C
 EXMOD single_pulse_dec
 OBRQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 512
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IIRNUC ¹H
 CTEMP 26.8 c
 SLVNT CDCl₃
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

single_pulse

DFILE 1016019minor-a-l.als
 COMNT single_pulse
 DATIM 14-12-2007 20:54:54
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFREQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTEMP 26.6 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 42

21.00

single pulse decoupled gated ^{13}C

DFILE: 1016019minor BCM-1.als
 COMNT single pulse decoupled gate
 DATIM 13-12-2007 22:51:48
 OBNUC ^{13}C
 EXMOD single pulse dec
 OBFREQ 125.77 MHz
 OBSET 7.87 kHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 512
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC ^1H
 CTEMP 26.9 c
 SLVNT CDCl_3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

single_pulse

DFILE 1016D181-1.als
 COMNT single_pulse
 DATIM 09-05-2008 20:21:21
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTEMP 26.2 c
 SLVT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 38

22.87

DFILE	1016D181	BCW512-1.a1s
COMNT	single pulse decoupled gate	
DATIM	09-05-2008	21:01:49
OBNUC	13C	
EXMOD	single_pulse_dec	
OBFRQ	125.77	MHz
OBSET	7.87	KHz
OBFIN	4.21	Hz
POINT	26214	
FREQU	31446.06	Hz
SCANS	500	
ACQTM	0.8336	sec
PD	2.0000	sec
PW1	3.83	usec
IRNUC	1H	
CTEMP	26.5	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	0.12	Hz
RGAIN	60

single_pulse

DFILE: 1016D182-1.als
 COMNT: single_pulse
 DATIM: 10-05-2008 18:22:42
 OBNUC: 1H
 EXMOD: single_pulse.ex2
 OBRFQ: 500.16 MHz
 OBSET: 2.41 KHz
 OBFIN: 6.01 Hz
 POINT: 13107
 FREQU: 7507.39 Hz
 SCANS: 8
 ACQTM: 1.7459 sec
 PD: 5.0000 sec
 PW1: 6.05 usec
 IRNUC: 1H
 CTEMP: 25.7 c
 SLVNT: CDCl3
 EXREF: 0.00 ppm
 BF: 0.12 Hz
 RGAIN: 38

20.56

single pulse decoupled gated NOE

DFILE 1016D182 BCM-1.als
 COMNT single pulse decoupled gate
 DATIM 10-05-2008 19:04:01
 OBNUC 13C
 EXMOD single_pulse_dec
 OBRQ 125.77 MHz
 OBSE 7.87 KHz
 OBFN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 500
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC 1H
 CTEMP 26.2 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

single_pulse

DFILE: 1016C160 080201 H-1.a1s
 COMNT single_pulse
 DATIM 01-02-2008 15:34:49
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBRFQ 500.16 MHz
 OBSST 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTMP 28.2 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 48

single pulse decoupled gated NOE

DFILE	1016050	080201	BCM-1.a1s
COMNT	single pulse decoupled gate		
DATIM	01-02-2008	21:37:25	
13C			
EXMOD	single_pulse_dec		
OBFRQ	125.77	MHz	
OBSET	7.87	KHz	
OBFIN	4.21	Hz	
POINT	26214		
FREQU	31446.06	Hz	
SCANS	512		
ACQTM	0.8336	sec	
PD	2.0000	sec	
PW1	3.83	usec	
1H			
IRNUC	26.7	c	
CTEMP			
SLVNT	CDCL3		
EXREF	77.00	ppm	
BF	0.12	Hz	
RGAIN	60

single_pulse

DFILE 10160113 080308-1.als
 COMNT single_pulse
 DATIM 08-03-2008 14:49:28
 OBNUC III
 EXMOD single_pulse.ex2
 OBFREQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IIRN III
 CTMP 25.8 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 40

single pulse decoupled gated NOE

DFILE: 10160113 080308 BCM-1.als
 COMNT single pulse decoupled gate
 DATIM 08-03-2008 15:37:47
 OBNUC ¹³C
 EXMOD single_pulse_dec
 OBFRQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 1000
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC ¹H
 CTMP 25.9 °C
 SLVNT CDCl₃
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

DFILE	1016D192-1.a1s
COMNT	single_pulse
DATIM	19-05-2008 10:45:05
ORNBUC	1H
EXMOD	single_pulse.ex2
OFBRFQ	500.16 MHz
OBSET	2.41 kHz
OFBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.05 usec
IRNUC	1H
CTEMP	22.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40

single pulse decoupled gated NMR

DFILE 1016D192BCM 080520-1.als
 COMNT single pulse decoupled gate
 DATIM 21-05-2008 00:29:35
 OBNUC 13C
 EXMOD single pulse dec
 OBFRQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 800
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC 1H
 CTEMP 26.2 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

single_pulse

DFILE: 1016D197-1.als
 COMNT: single_pulse
 DATIM: 22-05-2008 10:15:09
 OBNUC: ¹H
 EXMOD: single_pulse.ex2
 OBFRQ: 500.16 MHz
 OBSET: 2.41 KHz
 OBFIN: 6.01 Hz
 POINT: 13107
 FREQU: 7507.39 Hz
 SCANS: 8
 ACQTM: 1.7459 sec
 PD: 5.0000 sec
 PW1: 6.05 usec
 IRNUC: ¹H
 CTMP: 26.0 c
 SLVNT: CDCl₃
 EXREF: 0.00 ppm
 BF: 0.12 Hz
 RGAIN: 40

single pulse decoupled gated NOE

1016D197BCM-1.als
 COMNT single pulse decoupled gate
 DATIM 22-05-2008 11:40:09
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 1024
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC 1H
 CTEMP 26.8 c
 SLVNT CDCl3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

DFILE 1016C157-1Date.als
 COMNT
 DATIM Fri Oct 12 10:47:16 2007
 ORNUC 1H
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OFIN 10500.00 Hz
 POINT 32768
 FREQU 7992.01 Hz
 SCANS 8
 ACQTM 4.1001 sec
 PD 2.9000 sec
 5.50 usec
 PW1 1H
 IRNUC 1H
 CTEMP 22.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 14

single pulse decoupled gated NOE

DFILE 1016C157-1BCM-1.als
 COMNT single pulse decoupled gate
 DATIM 12-10-2007 13:37:16
 OBNUC 13C
 EXMOD single pulse dec
 OBFREQ 125.77 MHz
 OBSET 7.87 kHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 512
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC 1H
 CTEMP 24.6 c
 SLVNT CDCl3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

DFILE 1016C157-2Date.als
 COMNT
 DATIM Fri Oct 12 10:54:24 2007
 OBNUC 1H
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSET 124.00 kHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 7992.01 Hz
 SCANS 8
 ACQTM 4.1001 sec
 PD 2.9000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 22.9 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 16

single pulse decoupled gated NOE

144.64
135.58
133.83
133.52
129.79
129.56
128.53
126.72
125.78
123.94
119.70
118.07
116.29
112.18

77.26
77.00
76.74
65.73
62.53
56.79
43.95
39.39
27.03
21.52
18.02
11.98

DFILE 1016D55 BCM 080131-1.als
COMNT single pulse decoupled gate
DATIM 31-01-2008 14:09:23
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 kHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 300
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 28.1 c
SLVT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

single_pulse

DFILE 1016C166 080204-1.als
 COMNT single_pulse
 DATIM 04-02-2008 11:36:34
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTEMP 25.4 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 44

single pulse decoupled gated NOE

DFILE 1016C166 080204 BCM-1.als
COMNT single pulse decoupled gate
DATIM 04-02-2008 12:24:33
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1000
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 58

single_pulse

DFILE: 1016C159e 080626 550-100-1.
 COMNT single_pulse
 DATIM 26-06-2008 22:13:14
 OBNUC 1H
 EXMOD single_pulse;ex2
 OBRFQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTMP 21.5 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 50

single pulse decoupled gated NOE

DFILE 1016C159c BCM 550-100-1.als
 COMNT single pulse decoupled gate
 DATIM 05-06-2008 09:09:10
 OBNUC ¹³C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBSSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 12000
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IIRNUC ¹H
 CTEMP 26.8 c
 SLVNT CDCl₃
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 60

single_pulse

DFILE 1016D139-1 080318-1.als
 COMNT single_pulse
 DATIM 18-03-2008 10:52:09
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.05 usec
 IRNUC 1H
 CTEMP 26.0 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 42

single pulse decoupled gated NOE

171.20
144.91
143.74
137.75
135.35
134.06
133.41
130.00
129.92
129.61
128.31
126.74
125.75
120.66
120.40
117.23
115.92
113.11
77.25
77.00
76.74
52.98
52.32
40.76
40.18
29.43
21.55
21.53

DFILE 1016D139-1 BCM 080318-1.als
COMNT single pulse decoupled gate
DATIM 18-03-2008 11:46:19
OBNUC 13C
EXMOD single_pulse_dec
OBFREQ 125.77 MHz
OBSET 7.87 kHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 800
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

DFILE 1016D166 080715a.als
 COMNT
 DATIM Tue Jul 15 23:37:41 2008
 OBNUC ¹H
 EXMOD NON
 OBRQ 399.65 MHz
 OBSE 124.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 7992.01 Hz
 SCANS 8
 ACQTM 4.1001 sec
 PD 2.9000 sec
 PW1 5.50 usec
 IRNUC ¹H
 CTEMP 22.9 c
 SLVNT CDCl₃
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 23

single pulse decoupled gated NOE

DFILE 1016E10 080706 BCM-1.als
 COMNT single pulse decoupled gate
 DATIM 06-07-2008 17:07:38
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBSET 7.87 kHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 1600
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IIRNUC 1H
 CTEMP 24.3 c
 SLVNT CDCl3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 58

single_pulse

DFILE I016E23-2a pyridine-l.als

COMNT single_pulse
 DATIM 12-07-2008 15:55:15

OBNUC 1H
 EXMOD single_pulse.ex2

OBFRQ 500.16 MHz
 OBSET 2.41 KHz

OBFIN 6.01 Hz
 POINT 13107

FREQU 7507.39 Hz
 SCANS 32

ACQTM 1.7459 sec
 PD 5.0000 sec

PW1 6.05 usec
 IRNUC 1H

CTEMP 24.8 c
 SLVNT CD5N

EXREF 0.00 ppm
 BF 0.12 Hz

RGAIN 48

single pulse decoupled gated NOE

DFILE 1016E23-2 pyridine 080712 B
 COMNT single pulse decoupled gate
 DATIM 13-07-2008 00:23:45
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBFSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 2000
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.83 usec
 IRNUC 1H
 CTEMP 23.8 c
 SLVNT C5D5N
 EXREF 123.50 ppm
 BF 0.12 Hz
 RGAIN 58