Supplementary Material (ESI) for Chemical Communications

– Electronic Supplementary Information (ESI) –

(Experimental Procedures, Characterization Data, and Copies of ^{1}H and ^{13}C NMR Spectra)

Total Synthesis of (+)-Stachyflin: A Potential Anti-Influenza A Virus Agent

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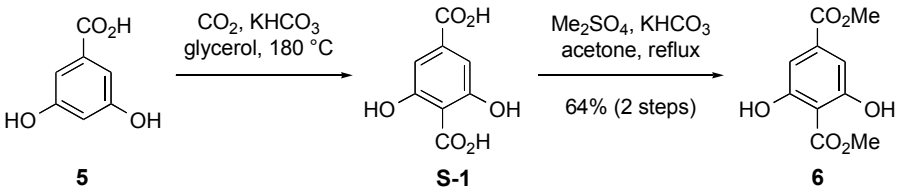
General Techniques.

All reactions involving air- and moisture-sensitive reagents were carried out using oven dried glassware and standard syringe-septum cap techniques. Routine monitorings of reaction were carried out using glass-supported Merck silica gel 60 F_{254} TLC plates. Flash column chromatography was performed on Kanto Chemical Silica Gel 60N (spherical, neutral 40–50 nm) with the solvents indicated.

All solvents and reagents were used as supplied with following exceptions. Tetrahydrofuran (THF) was freshly distilled from Na metal/benzophenone under argon. MeOH and EtOH were distilled from Na metal under argon. *N*,*N*-Dimethylformamide (DMF), hexamethylphosphorous triamide (HMPA), MeCN, benzene, and CH_2Cl_2 were distilled from calcium hydride under argon.

Measurements of optical rotations were performed with a JASCO DIP-370 automatic digital polarimeter. Melting points were taken on a Yanaco MP-3 micro melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a JEOL AL-400 (400 MHz) spectrometer. Chemical shifts were expressed in ppm using Me_4Si (δ=0) as an internal standard. The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), and broad (br). Infrared (IR) spectral measurements were carried out with a JASCO FT/IR-4100 spectrometer. Low- and High-resolution mass (HRMS) spectra were measured on a JEOL JMS-DX 303/JMA-DA 5000 SYSTEM high resolution mass spectrometer.

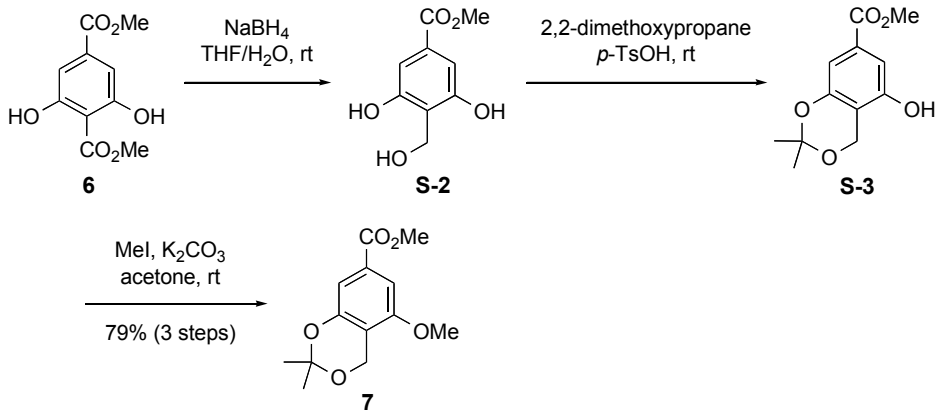
Dimethyl 2,6-dihydroxyterephthalate (6)



A stirred suspension of 3,5-dihydroxybenzoic acid (**5**) (50.0 g, 0.32 mol) in glycerol (100 mL) was heated at 100 °C for 1 h. After cooling, $KHCO_3$ (150 g, 1.5 mol) was added in small portions to the mixture, and the resulting suspension was heated at 180 °C under CO_2 for 3h. After cooling, hot water (300 mL) and concentrated HCl (300 mL) were added to the mixture, and the resulting mixture was extracted with Et_2O (6 x 300 mL). The combined extracts were washed with brine (3 x 200 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a pale yellow solid, which was purified by recrystallization (MeOH) to give 2,6-dihydroxyterephthalic acid (**S-1**) (45.4 g) as a pale yellow fine powder, mp 268–269 °C. This material was used for the next reaction.

Me_2SO_4 (54.2 mL, 0.57 mol) was added dropwise to a stirred solution of **S-1** (45.4 g, 0.23 mol) in acetone (500 mL) containing $KHCO_3$ (57.0 g, 0.57 mol) at room temperature, and the mixture was heated at reflux for 10 h. After cooling, the mixture was concentrated in vacuo to give a residue, which was diluted with saturated aqueous $NaHCO_3$ (300 mL). The resulting mixture was extracted with CH_2Cl_2 (4 x 300 mL). The combined extracts were washed with brine (2 x 200 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a pale yellow solid, which was purified by recrystallization (MeOH) to give **6** (47.0 g, 64%, 2 steps) as pale yellow prisms, mp 146–149 °C. IR (KBr): 1720, 1674, 1637, 1572, 1419, 1345, 1224, 1172, 1066, 1000, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ9.67 (2H, br s), 7.11 (2H, s), 4.11 (3H, s), 3.91 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ169.5, 165.7, 160.7 (2 C), 137.1, 109.1 (2 C), 102.8, 53.2, 52.5; HRMS (EI) calcd for $C_{10}H_{10}O_6$ (M^+) 226.0477, found 226.0479.

Methyl 5-methoxy-2,2-dimethyl-4*H*-benzo[*d*][1,3]dioxine-7-carboxylate (7)



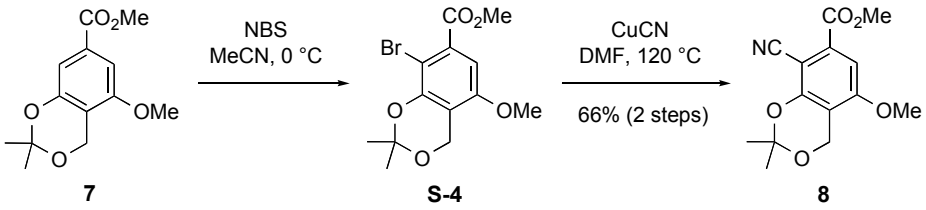
$NaBH_4$ (9.04 g, 0.24 mol) in water (150 mL) was added dropwise to a stirred solution of **6** (27.0 g, 0.12 mol) in THF (600 mL) at 0 °C. After 1 h, the reaction was quenched with 1 M HCl (100 mL) at 0 °C, and the resulting mixture was extracted with EtOAc (4 x 200 mL). The combined extracts were washed with brine (2 x 100 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by short-pass column chromatography (EtOAc) to give methyl 3,5-dihydroxy-4-(hydroxymethyl)benzoate (**S-2**) (23.7 g), which was used for the next reaction without further purification.

p-TsOH·H_2O (1.14 g, 6.0 mmol) was added to a stirred solution of **S-2** (23.7 g, 0.12 mol) in 2,2-dimethoxypropane (300 mL) at room temperature. After 5 h, the mixture was concentrated in vacuo to afford a residue, which was diluted with saturated aqueous $NaHCO_3$ (100 mL) at 0 °C. The resulting mixture was extracted with EtOAc (3 x 200 mL). The combined extracts were washed with brine (2 x 100 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by short-pass column chromatography (hexane/EtOAc 2:1) to give methyl 5-hydroxy-2,2-dimethyl-4*H*-benzo[*d*][1,3]dioxine-7-carboxylate (**S-3**) (24.3 g) as a colorless amorphous powder, which was used for the next reaction without further purification.

MeI (13.3 mL, 0.22 mol) was added to a stirred solution of **S-3** (24.3 g, 0.10 mol) in acetone (250 mL) containing K_2CO_3 (26.5 g, 0.19 mol) at room temperature. After 12 h, the mixture was concentrated in vacuo to afford a residue, which was then diluted with water (200 mL). The resulting mixture was extracted with EtOAc (3 x 200 mL). The combined extracts were washed with brine (2 x 100 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 10:1) to give **7** (23.8 g, 73%, 3 steps) as a pale yellow viscous liquid. IR (KBr): 1720, 1674, 1637, 1572, 1419, 1345, 1224, 1172, 1066, 1000, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (1H, s),

7.09 (1H, s), 4.78 (2H, s), 3.89 (3H, s), 3.86 (3H, s), 1.53 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 150.4, 147.6, 140.4, 123.3, 107.0, 106.2, 88.3, 74.4, 56.1, 51.5, 23.2 (2 C); HRMS (EI) calcd for $C_{13}H_{16}O_5$ (M^+), 252.0998, found 252.0998.

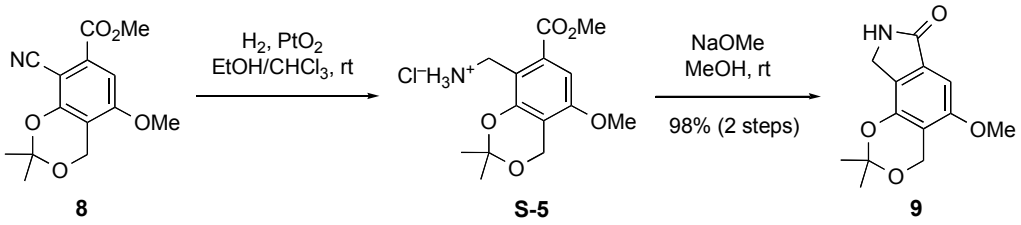
Methyl 8-cyano-5-methoxy-2,2-dimethyl-4*H*-benzo[*d*][1,3]dioxine-7-carboxylate (8)



N-bromosuccinimide (NBS) (13.3 g, 75 mmol) was added in small portions to a stirred solution of **7** (14.5 g, 58 mmol) in dry MeCN (350 mL) at 0 °C. After 4 h, the reaction was quenched with 1 M NaOH (100 mL) at 0 °C, and the resulting mixture was extracted with EtOAc (4 x 200 mL). The combined extracts were washed with brine (2 x 100 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by short-pass column chromatography (hexane/EtOAc 3:1) to give methyl 8-bromo-5-methoxy-2,2-dimethyl-4*H*-benzo[*d*][1,3]dioxine-7-carboxylate (**S-4**) (18.8 g) as a pale yellow solid, which was used for the next reaction without further purification.

CuCN (15.3 g, 0.17 mol) was added to a stirred solution of **S-4** (18.8 g, 57 mmol) in dry DMF (200 mL) at room temperature, and the mixture was heated at 120 °C for 40 min. After cooling, a solution of NaCN (47.0 g, 0.96 mol) in water (300 mL) was added to the above mixture at room temperature. After 3 h, the mixture was extracted with EtOAc (5 x 250 mL). The combined extracts were washed with brine (2 x 200 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by recrystallization (hexane/EtOAc) to give **8** (10.5 g, 66%, 2 steps) as a pale yellow amorphous solid. IR (KBr): 2222, 1718, 1593, 1462, 1423, 1383, 1363, 1336, 1282, 1249, 1201, 1142, 1111, 1065, 1038, 1020, 860, 833, 785 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (1H, s), 4.75 (2H, s), 3.96 (3H, s), 3.90 (3H, s), 1.57 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 158.1, 155.5, 133.5, 114.4, 112.8, 104.7, 101.6, 94.4, 57.5, 56.1, 52.3, 24.6, 24.5; HRMS (FAB) calcd for $C_{14}H_{15}NO_5$ (M^+), 277.0950, found 277.0950.

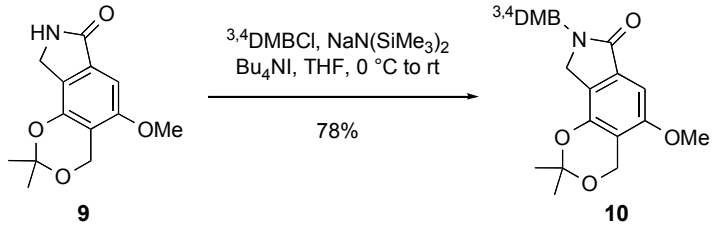
5-Methoxy-2,2-dimethyl-8,9-dihydro-[1,3]dioxino[4,5-*e*]isoindol-7(4*H*)-one (9)



PtO_2 (2.00 g) was added to a solution of **8** (8.14 g, 29 mmol) in EtOH/$CHCl_3$ 3:1 (300 mL) at room temperature. The mixture was stirred for 24 h under H_2 (1 atm) at room temperature. The reaction mixture was diluted with EtOH (200 ml), and the catalyst was filtered off through a small pad of Celite®. Concentration of the filtrate in vacuo afforded methyl 8-(aminomethyl)-5-methoxy-2,2-dimethyl-4*H*-benzo[*d*][1,3]dioxine-7-carboxylate hydrochloride salt (**S-5**) (7.57 g) as a white solid, which was used for the next reaction without purification.

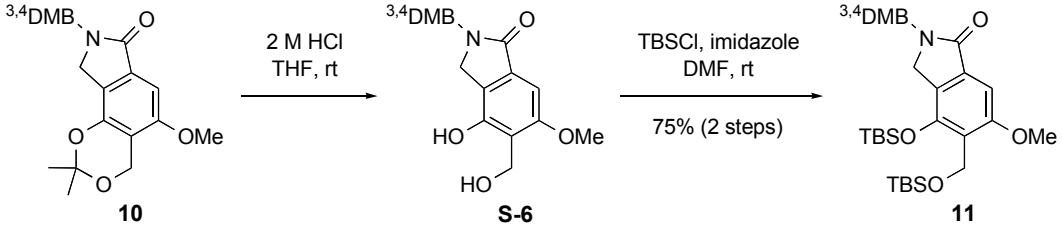
A solution of NaOMe in MeOH (25% w/v solution, 15.4 mL, 75 mmol) was added to a stirred solution of **S-4** (7.57 g, 25 mmol) in MeOH (300 ml) at room temperature. After 1 h, the mixture was concentrated in vacuo to give a residue, which was diluted with water (400 mL). The resulting mixture was extracted with EtOAc (5 x 150 mL). The combined extracts were washed with brine (2 x 100 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:1 to 0:1) to give **9** (7.17 g, 98%, 2 steps) as a pale yellow solid. Recrystallization from EtOAc afforded colorless prisms, mp 205–207 °C. IR (KBr): 3200, 2227, 1696, 1628, 1607, 1477, 1374, 1354, 1108, 839, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (1H, br s), 6.93 (1H, s), 4.84 (2H, s), 4.31 (2H, s), 3.87 (3H, s), 1.56 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 156.5, 146.9, 132.3, 123.9, 111.9, 96.3, 66.89, 58.5, 55.5, 42.8, 24.6 (2 C); HRMS (FAB) calcd for $C_{13}H_{15}NO_4$ (M^+), 249.1001, found 249.0989.

8-(3,4-Dimethoxybenzyl)- 2,2-dimethyl-8,9-dihydro-[1,3]dioxino[4,5-*e*]isoindol-7(4*H*)-one (10)



$NaN(SiMe_3)_2$ in THF (1.9 M solution, 12.7 mL, 24 mmol) was added dropwise to a stirred solution of **9** (4.00 g, 16 mmol) in dry THF (100 mL) containing Bu_4NI (1.78 g, 4.8 mmol) at 0 °C under argon. After 1 h, a solution of 3,4-dimethoxybenzyl chloride (^{3,4}DMBCl) (5.17 g, 24 mmol) in dry THF (20 mL) was added dropwise to the above mixture at 0 °C, and stirring was continued for 48 h at room temperature. The reaction was quenched with H_2O (30 mL) at 0 °C, and the resulting mixture was extracted with EtOAc (4 x 100 mL). The combined extracts were washed with brine (2 x 60 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:3) to give **10** (5.02 g, 78%) as a white amorphous powder. IR (KBr): 1689, 1477, 1458, 1373, 1317, 1263, 1234, 1200, 1140, 1107, 1078, 1025, 862, 833, 810, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (1H, s), 6.81–6.85 (3H, m), 4.81 (2H, s), 4.71 (2H, s), 4.12 (2H, s), 3.87 (3H, s), 3.86 (3H, s), 3.85 (3H, s), 1.51 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 156.4, 149.3, 148.6, 146.8, 132.9, 129.8, 121.5, 120.6, 111.5, 111.4, 111.0, 99.9, 96.6, 58.5, 55.9 (2 C), 55.8, 46.7, 46.4, 24.6 (2 C); HRMS (FAB) calcd for $C_{22}H_{25}NO_6$ (M^+), 399.1682, found 399.1681.

4-(*tert*-Butyldimethylsiloxy)-5-(*tert*-butyldimethylsiloxy)methyl-2-(3,4-dimethoxybenzyl)-6-methoxy-isoindolin-1-one (11)

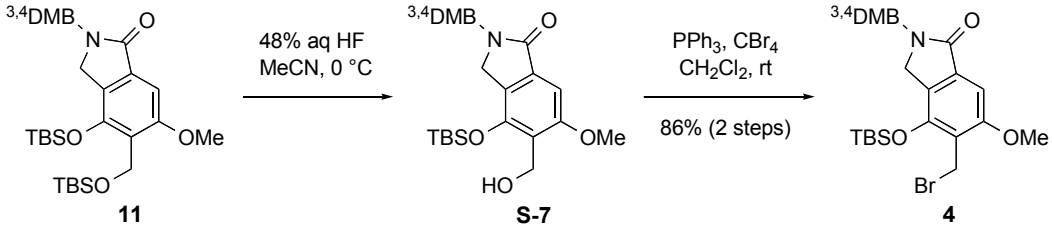


2 M HCl (50 mL) was added dropwise to a stirred solution of **10** (4.42 g, 11 mmol) in THF (100 mL) at room temperature. After 12 h, the mixture was diluted with saturated aqueous $NaHCO_3$ (100 mL) at 0 °C, and the resulting mixture was extracted with EtOAc (3 x 100 mL). The combined extracts were washed with

brine (2 x 80 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded 2-(3,4-dimethoxybenzyl)-4-hydroxy-5-hydroxymethyl-6-methoxyisoindolin-1-one (**S-6**) (3.98 g) as a colorless viscous liquid, which was used for the next reaction without purification.

tert-Butyldimethylsilyl chloride (TBSCl) (6.67 g, 44 mmol) was added to a stirred solution of **S-6** (3.98 g, 11 mmol) in dry DMF (100 mL) in the presence of imidazole (3.40 g, 50 mmol) at room temperature. After 24 h, the reaction was diluted with saturated aqueous NH_4Cl (150 mL) at room temperature, and the resulting mixture was extracted with EtOAc (3 x 200 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ (2 x 100 mL) and brine (2 x 50 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 3:1) to give **11** (4.88 g, 75%, 2 steps) as a colorless amorphous powder. IR (neat): 2954, 2931, 2894, 2857, 1691, 1617, 1594, 1515, 1470, 1433, 1258, 1130, 1063, 835, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.92 (1H, s), 6.66 (3H, s), 4.55 (2H, s), 4.54 (2H, s), 3.95 (2H, s), 3.72 (3H, s), 3.71 (3H, s), 3.69 (3H, s), 0.83 (9H, s), 0.72 (9H, s), 0.00 (6H, s), −0.08 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 160.2, 149.4, 149.2, 148.5, 133.7, 129.6, 124.3, 123.8, 120.3, 111.2, 111.1, 99.3, 55.8, 55.7, 55.5, 54.4, 48.0, 46.2, 25.8 (6 C), 18.5, 18.4, −3.9 (2 C), −5.4 (2 C); HRMS (EI) calcd for $C_{31}H_{49}NO_6Si_2$ (M^+), 587.3098, found 587.3096.

5-Bromomethyl-4-(*tert*-butyldimethylsiloxy)- 2-(3,4-dimethoxybenzyl)-6-methoxyisoindolin-1-one (4)

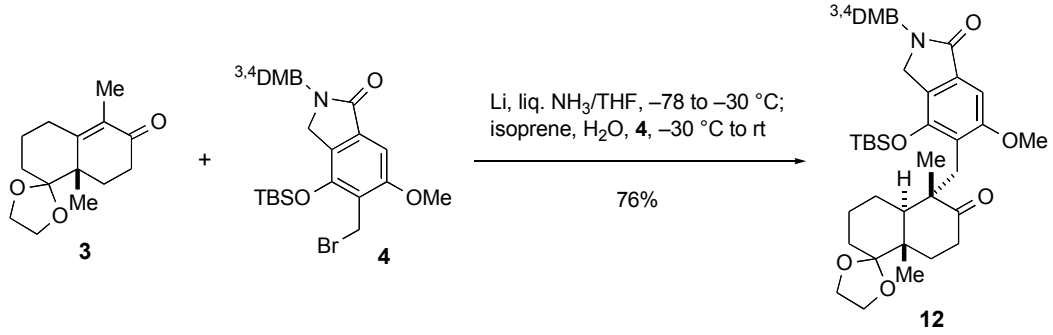


48% aqueous HF (0.15 mL, 3.6 mmol) was added slowly to a stirred solution of **11** (690 mg, 1.2 mmol) in MeCN (15 mL) at 0 ºC. After 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$ (6 mL), and the resulting mixture was extracted with EtOAc (3 x 20 mL). The combined extracts were washed with brine (2 x 10 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:1) to give **S-7** (491 mg) as a white solid. This product was used for the next reaction without further purification.

PPh_3 (408 mg, 1.6 mmol) was added to a stirred solution of **S-7** (491 mg, 1.0 mmol) and CBr_4 (1.03 g, 3.1 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After 3 h, the reaction was quenched with water (30 mL) at 0 °C, and the mixture was extracted with CH_2Cl_2 (3 x 30 mL). The combined extracts were dried over Na_2SO_4.

Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:1) to give **4** (540 mg, 86%, 2 steps) as a colorless amorphous powder. IR (KBr): 2955, 2932, 2858, 2837, 2251, 1695, 1681, 1617, 1593, 1515, 1470, 1435, 1257, 1157, 1139, 1078, 912, 833, 731, 765, 731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.88 (1H, s), 6.62 (3H, s), 4.50 (2H, s), 4.41 (2H, s), 3.91 (2H, s), 3.75 (3H, s), 3.66 (3H, s), 3.64 (3H, s), 0.82 (9H, s), 0.00 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 159.5, 149.2, 149.1, 148.6, 134.6, 129.3, 123.5, 121.3, 120.4, 111.2, 111.1, 99.6, 56.3, 55.8 (2 C), 47.9, 46.3, 25.7 (3 C), 23.5, 18.6, −3.5 (2 C); HRMS (EI) calcd for $C_{25}H_{34}BrNO_5Si$ (M^+), 535.1389, found 535.1387.

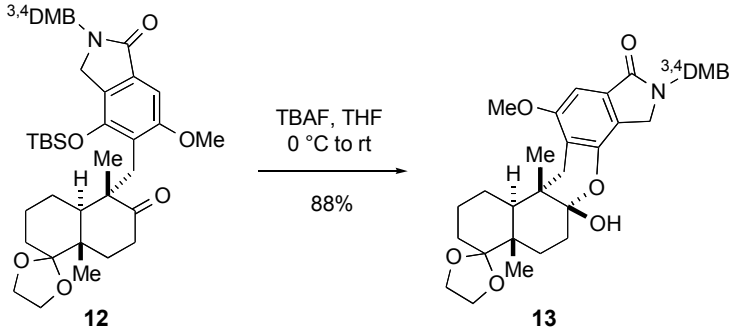
4-(*tert*-Butyldimethylsiloxy)-2-(3,4-dimethoxybenzyl)-6-methoxy-5-{[(4a′*S*,5′*S*,8a′*S*)-5′,8a′-dimethyl-6′-oxooctahydro-2′*H*-spiro[[1,3]dioxolane-2,1′-naphthalene]-5′-yl]methyl}-isoindolin-1-one (12)



(*S*)-5′,8a′-Dimethyl-3′,4′,8′,8a′-tetrahydro-2′*H*-spiro[[1,3]dioxolane-2,1′-naphthalen]-6′(7′*H*)-one (**3**) (94.4 mg, 0.4 mmol) in dry THF (2.0 mL) was added dropwise to a stirred solution of Li metal (14.0 mg, 2.0 mmol) in liquid NH_3 (10 mL) at −78 °C under argon. The resulting solution was allowed to warm at reflux (−30 °C) of liquid NH_3 for 1 h. A solution of **4** (535 mg, 1.0 mmol) in dry THF (3.0 mL) was added slowly to the above mixture at −30 °C. The reaction mixture was allowed to stand for 5 h at room temperature in order to evaporate off NH_3. After addition of saturated aqueous NH_4Cl (5 mL), the resulting mixture was extracted with EtOAc (3 x 40 mL). The combined extracts were washed with brine (2 x 20 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:2) to give **12** (210 mg, 76%) as a colorless amorphous powder. $[\alpha]_D^{25}$ +9.2 (*c* 3.12, $CHCl_3$); IR (KBr): 2935, 1689, 1595, 1516, 1466, 1435, 1329, 1257, 1184, 1136, 1082, 1026, 949, 908, 831, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.93 (1H, s), 6.74 (3H, d, J = 5.8 Hz), 4.78 (1H, d, J = 14.7 Hz), 4.63 (1H, d, J = 14.7 Hz), 4.08 (2H, s), 3.89–3.95 (4H, m), 3.87 (3H, s), 3.85 (3H, s), 3.73 (3H, s), 3.12 (1H, d, J = 13.4 Hz), 2.82 (1H, d, J = 13.6 Hz), 2.76–2.83 (1H, m), 2.29 (1H, quint, J = 7.3 Hz), 2.09–2.16 (2H, m), 1.61–1.63 (1H, m), 1.42–1.57 (4H, m), 1.37 (1H, dq, J = 12.8, 3.2 Hz), 1.26–1.31 (1H,

m), 0.99 (3H, s), 0.95 (9H, s), 0.91 (3H, s), 0.14 (3H, s), 0.07 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.2, 168.5, 159.5, 149.5, 149.3, 148.5, 133.0, 132.5, 131.9 (2 C), 129.7, 124.2, 122.0, 120.4, 111.2, 111.1, 99.1, 65.1, 64.7, 55.9 (2 C), 55.0, 51.3, 48.1, 46.7, 46.3, 42.1, 34.8, 34.3, 29.7, 29.1, 25.8 (3 C), 22.9, 22.7, 18.6, −2.8, −3.6; HRMS (EI) calcd for $C_{39}H_{55}NO_8Si$ (M^+), 693.3697, found 693.3676.

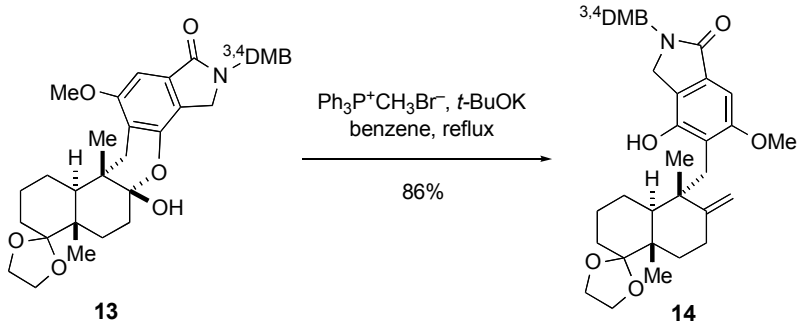
(4a*R*,6a*S*,10a*S*,10b*S*)-2-(3,4-Dimethoxybenzyl)-4a-hydroxy-12-methoxy-6a,10b-dimethyl-2,3,4a,5,6a,7,8,9,10,10a,10b-dodecahydrobenzo[*f*]chromano[2,3-*e*]isoindol-1,7-dione-7-ethyleneacetal (13)



Tetrabutylammonium fluoride (TBAF) in THF (1.0 M solution, 1.0 mL, 1.0 mmol) was added dropwise to stirred solution of **12** (162 mg, 0.23 mmol) in THF (20 mL) at 0 °C, and stirring was continued for 30 min at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (5 mL) at 0 °C, and the resulting mixture was extracted with EtOAc (3 x 30 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ (2 x 20 mL) and brine (2 x 20 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:2) to give **13** (119 mg, 88%) as a colorless viscous liquid. $[\alpha]_D^{25}$ −37.1 (*c* 2.36, $CHCl_3$); IR (neat): 3316, 2938, 1667, 1606, 1514, 1472, 1438, 1414, 1317, 1260, 1106, 1026, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77–6.89 (4H, m), 4.64 (1H, d, J = 14.1 Hz), 4.55 (1H, d, J = 14.1 Hz), 3.90–4.12 (4H, m), 3.83 (3H, s), 3.82 (3H, s), 3.81 (3H, s), 2.89 (1H, br s), 2.52 (1H, d, J = 17.1 Hz), 2.39 (1H, d, J = 17.1 Hz), 1.99–2.09 (3H, m), 1.50–1.68 (6H, m), 1.12–1.42(4H, m), 1.11 (3H, s), 0.80 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 158.6, 149.2, 148.6, 146.8, 130.9, 129.8, 121.3, 120.7, 115.9, 113.0, 111.6, 111.0, 99.6, 97.1, 65.3, 64.7, 55.9, 55.8, 55.6, 46.9, 46.3, 45.1, 43.1, 37.8, 31.5, 30.3, 29.2, 26.8, 22.9, 20.3, 17.4, 16.9; HRMS (EI) calcd for $C_{33}H_{41}NO_8$ (M^+), 579.2832, found 579.2827.

2-(3,4-Dimethoxybenzyl)-4-hydroxy-6-methoxy-5-{[(4a′*S*,5′*S*,8a′*S*)-5′,8a′-dimethyl-6′-(methylene)-

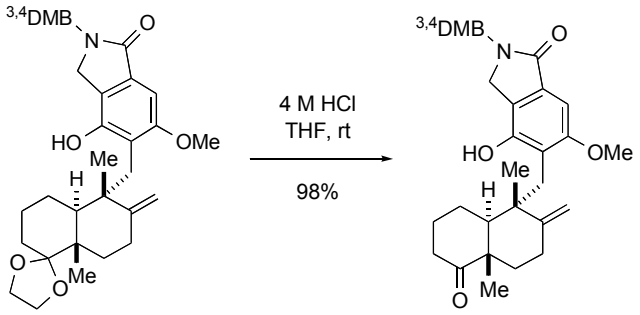
octahydro-2′*H*-spiro[[1,3]dioxolane-2,1′-naphthalene]-5′-yl]methyl}isoindolin-1-one (14)



A stirred suspension of *t*-BuOK (232 mg, 2.1 mmol) and $Ph_3P^+CH_3Br^-$ (740 mg, 2.1 mmol) in dry benzene (30 mL) was heated at reflux for 2 h under argon, and then roughly half volume of the solvent was evaporated off. After cooling, a solution of **13** (120 mg, 0.21 mmol) in dry benzene (10 mL) was added to the above mixture, and the resulting solution was refluxed for 3 h under argon. After cooling, the reaction was quenched with water (5 mL), and the mixture was extracted with EtOAc (3 x 40 mL). The combined extracts were washed with brine (2 x 30 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:3) to give **14** (103 mg, 86%) as a colorless viscous liquid. $[\alpha]_D^{25}$ +91.1 (*c* 0.97, $CHCl_3$); IR (neat): 2935, 1653, 1593, 1516, 1466, 1437, 1415, 1335, 1259, 1238, 1182, 1138, 1072, 1026, 949, 906, 750, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.99 (1H, s), 6.85–6.88 (2H, m), 6.80–6.83 (1H, m), 6.16 (1H, s), 4.93 (2H, d, *J* = 18.4 Hz), 4.73 (1H, d, *J* = 14.6 Hz), 4.67 (1H, d, *J* = 14.5 Hz), 4.13 (2H, s), 3.89–3.95 (3H, m), 3.87 (1H, d, *J* = 1.4 Hz), 3.86 (3H, s), 3.85 (3H, s), 3.84 (3H, s), 2.97 (1H, d, *J* = 13.7 Hz), 2.68 (1H, d, *J* = 13.7 Hz), 2.12–2.17 (2H, m), 2.03–2.06 (1H, m), 2.00 (1H, dd, *J* = 2.8, 11.7 Hz), 1.79–1.81 (1H, m), 1.71 (1H, d, *J* = 7.9 Hz), 1.63 (1H, s), 1.43–1.57 (4H, m), 1.10 (3H, s), 1.00 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 160.0, 151.0, 149.3, 148.6, 132.5, 129.9, 120.8, 117.9, 113.4, 111.6, 111.1, 108.7, 97.8, 86.6, 64.8, 64.6, 64,4, 56.0 (2 C), 55.9 (2 C), 55.8, 47.2, 46.5 (2 C), 43.7, 42.5, 32.1, 30.5, 29.4, 22.9, 22.7, 21.4; HRMS (EI) calcd for $C_{34}H_{43}NO_7$ (M^+), 577.3039, found 577.3037.

2-(3,4-Dimethoxybenzyl)-4-hydroxy-6-methoxy-5-{[(1*S*,4a*S*,8a*S*)-1,4a-dimethyl-2-methylene-5-

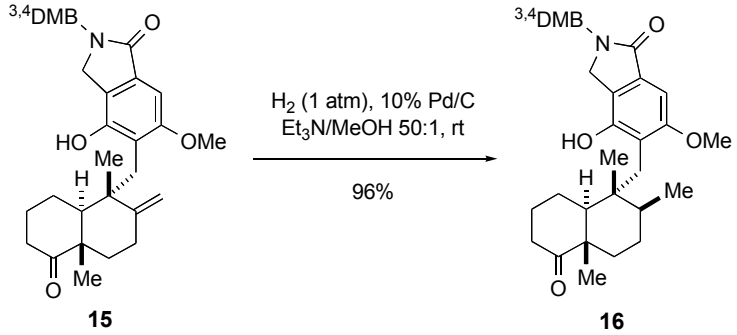
oxodecahydronaphthalen-1-yl]methyl}isoindolin-1-one (15)



14 **15**

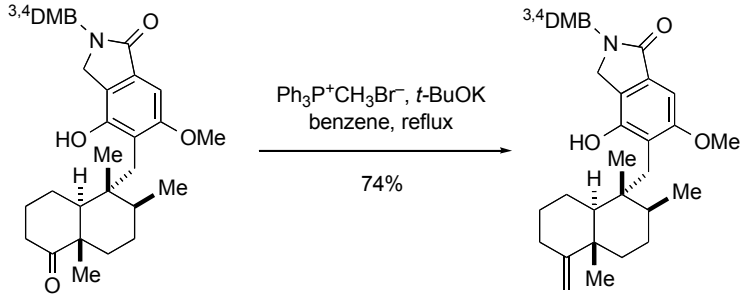
4 M HCl (3.0 mL) was added to a stirred solution of **14** (77.0 mg, 0.13 mmol) in THF (15 mL) at room temperature. After 17 h, the reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL), and the resulting mixture was extracted with EtOAc (3 x 30 mL). The combined extracts were washed with brine (2 x 20 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc, 1:3) to give **15** (69.7 mg, 98%) as a colorless viscous oil. $[\alpha]_D^{25}$ +45.8 (*c* 3.17, $CHCl_3$); IR (neat): 2970, 2943, 1734, 1716, 1684, 1558, 1541, 1508, 1458, 1363, 1230, 1217, 1134, 1026, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.97 (1H, s), 6.83–6.88 (2H, m), 6.80–6.82 (1H, m), 6.27 (1H, s), 5.04 (2H, d, J = 11.6 Hz), 4.69 (2H, d, J = 2.5 Hz), 4.13 (2H, d, J = 2.0 Hz), 3.86 (3H, s), 3.84 (3H, s), 3.82 (3H, s), 3.09 (1H, d, J = 14.0 Hz), 2.61 (1H, d, J = 14.1 Hz), 2.51 (1H, dt, J = 14.4, 6.3 Hz), 2.36–2.45 (1H, m), 2.22–2.30 (2H, m), 2.04–2.13 (3H, m), 1.76–1.83 (2H, m), 1.71 (1H, s), 1.50 (1H, dq, J = 13.6, 4.0 Hz), 1.26 (3H, s), 1.08 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.6, 168.5 159.7, 151.3, 149.3, 148.6, 132.8, 129.8, 121.4, 120.7, 117.0, 111.6, 111.1, 109.5, 97.7, 56.0 (2 C), 55.9 (2 C), 55.8, 48.9 (2 C), 47.1, 46.5 (2 C), 44.3, 38.1, 31.0, 29.5, 25.3, 23.4, 23.1; HRMS (EI) calcd for $C_{32}H_{39}NO_6$ (M^+), 533.2777, found 533.2781.

2-(3,4-Dimethoxybenzyl)-4-hydroxy-6-methoxy-5-{[(1*R*,2*S*,4a*S*,8a*S*)-1,2,4a-trimethyl-5-oxodecahydro-naphthalen-1-yl]methyl}isoindolin-1-one (16)



10% Pd/C (70.0 mg) was added to a solution of **15** (69.7 mg, 0.13 mmol) in Et_3N/MeOH 50:1 (5 mL), and the mixture was stirred for 24 h under H_2 (1 atm) at room temperature. The mixture was diluted with MeOH (30 mL), and the catalyst was filtered off through a small pad of Celite®. Concentration of the filtrate in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:1) to give **16** (67.1 mg, 96%) as a colorless viscous liquid. $[\alpha]_D^{25}$ −0.15 (*c* 2.74, $CHCl_3$); IR (neat): 2936, 1659, 1592, 1515, 1466, 1436, 1260, 1139, 1073, 1026, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ6.96 (1H, s), 6.83–6.86 (2H, m), 5.16 (1H, s), 4.73 (1H, d, *J* = 14.7 Hz), 4.68 (1H, d, *J* = 14.6 Hz), 4.15 (2H, s), 3.86 (3H, s), 3.84 (3H, s), 3.81 (3H, s), 2.74 (1H, d, *J* = 14.4 Hz), 2.68 (1H, d, *J* = 14.4 Hz), 2.57 (1H, td, *J* = 14.0, 7.3 Hz), 2.16 (1H, dd, *J* = 14.2, 5.1 Hz), 2.00–2.10 (2H, m), 1.70 (1H, dq, *J* = 13.2, 3.4 Hz), 1.33–1.53 (5H, m), 1.22–1.31 (2H, m), 1.14 (3H, s), 0.95 (3H, s), 0.89 (3H, d, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 216.6, 169.0, 160.3, 151.0, 149.3, 148.6, 131.8, 129.6, 120.7, 120.5, 119.4, 111.4, 111.2, 97.3, 55.9 (2 C), 55.5, 50.6, 49.7, 47.5, 46.4, 43.6, 38.5, 37.5, 35.1, 32.3, 27.6, 26.0, 22.7, 18.8, 18.4, 17.0; HRMS (EI) calcd for $C_{32}H_{41}NO_6$ (M^+), 535.2777, found 535.2938.

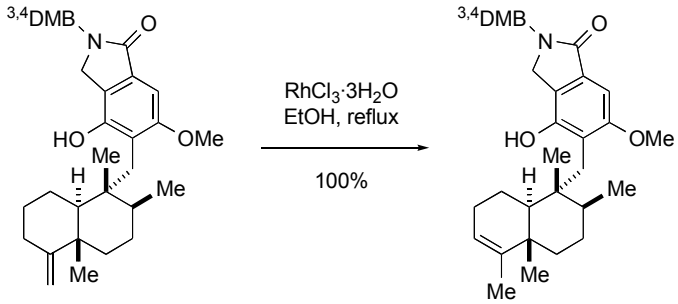
2-(3,4-Dimethoxybenzyl)-4-hydroxy-6-methoxy-5-{[(1*R*,2*S*,4a*S*,8a*S*)-1,2,4a-trimethyl-5-(methylene)-decahydronaphthalen-1-yl]methyl}isoindolin-1-one (17)



16 **17**

A stirred suspension of potassium *t*-BuOK (0.31g, 2.8 mmol) and $Ph_3P^+CH_3Br^-$ (0.99 g, 2.8 mmol) in dry benzene (80 mL) was heated at reflux for 2 h under argon, and then roughly half volume of the solvent was evaporated off. A solution of **16** (74.0 mg, 0.14 mmol) in dry benzene (20 mL) was added slowly to the above mixture, and the resulting solution was then refluxed for 5 h under argon. The reaction was quenched with water (10 mL) at 0 °C, and the mixture was extracted with EtOAc (3 x 40 mL). The combined extracts were washed with brine (2 x 20 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:2) to give **17** (54.6 mg, 74%) as a colorless viscous liquid. $[\alpha]_D^{25}$ −7.5 (*c* 2.72, $CHCl_3$); IR (neat): 2931, 2857, 2253, 1654, 1592, 1515, 1466, 1436, 1260, 1138, 1027, 910, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.90 (1H, s), 6.74–6.80 (3H, m), 5.79 (1H, s), 4.65 (2H, d, J = 4.9 Hz), 4.42 (2H, d, J = 10.7 Hz), 4.15 (1H, s), 4.09 (2H, dd, J = 14.1, 7.3 Hz), 3.82 (3H, s), 3.80 (3H, s), 3.77 (3H, s), 2.02–2.06 (1H, m), 1.14–1.48 (12H, m), 1.01 (3H, s), 0.85 (3H, s), 0.81 (3H, d, J = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 160.3, 159.9, 150.7, 149.2, 148.5, 131.7, 129.7, 120.6, 120.5, 119.4, 111.4, 111.1, 102.8, 97.2, 55.9, 55.5 (2 C), 51.8, 47.4, 46.4, 43.3, 40.6, 39.2, 36.5, 35.4, 32.9, 28.7, 28.5, 23.9, 20.4, 18.4, 16.4; HRMS (EI) calcd for $C_{33}H_{43}NO_5$ (M^+), 533.3141, found 533.3148.

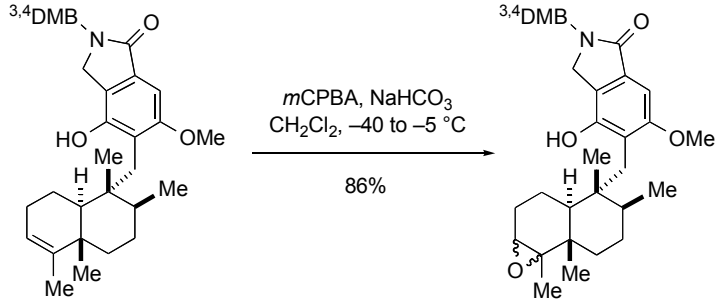
2-(3,4-Dimethoxybenzyl)-4-hydroxy-6-methoxy-5-{[(1*R*,2*S*,4a*S*,8a*S*)-1,2,4a,5-tetramethyl-1,2,3,4,4a,7,8,8a-octahydronaphthalen-1-yl]methyl}isoindolin-1-one (18)



17 **18**

A mixture of **17** (48.0 mg, 90 μmol) and $RhCl_3 \cdot 3H_2O$ (4.0 mg, 18 mmol) in EtOH (6 mL) was heated at reflux for 24 h. After cooling, the mixture was diluted with MeOH (60 mL), and the catalyst was filtered off through a small pad of Celite®. Concentration of the filtrate in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:2) to give **18** (48.0 mg, 100%) as a colorless viscous liquid. $[\alpha]_D^{25}$ +14.2 (*c* 3.24, $CHCl_3$); IR (neat): 2935, 1658, 1592, 1515, 1466, 1436, 1416, 1260, 1239, 1137, 1074, 1027, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.85 (1H, s), 6.64–6.72 (3H, m), 5.03 (1H, s), 4.57 (2H, s), 4.15 (2H, s), 3.74 (3H, s), 3.71 (6H, s), 2.74 (1H, d, *J* = 14.1 Hz), 2.60 (1H, d, *J* = 14.1 Hz), 1.80–189 (3H, m), 1.44 (3H, s), 1.31–1.55 (3H, m), 1.12–1.23 (3H, m), 0.98 (3H, s), 0.78–1.09 (2H, m), 0.78 (3H, s), 0.69 (3H, d, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 160.2, 150.7, 149.2, 148.5, 144.3, 131.6, 129.7, 120.6, 120.5, 120.4, 119.8, 111.4, 111.1, 97.3, 55.9, 55.5, 49.9, 47.4, 46.4, 43.1, 39.5, 38.7, 38.3, 35.9, 35.6, 28.5, 27.2, 20.5, 20.0, 18.1, 17.9, 16.1; HRMS (EI) calcd for $C_{33}H_{43}NO_5$ (M^+), 533.3141, found 533.3137.

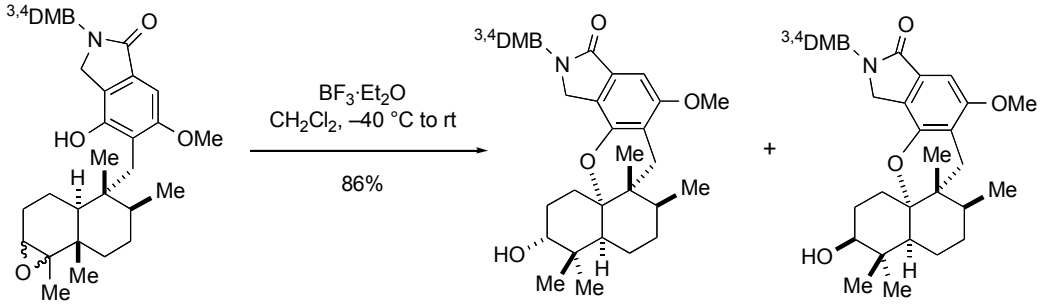
2-(3,4-Dimethoxybenzyl)-4-hydroxy-6-methoxy-5-{[(1a*RS*,3a*S*,4*R*,5*S*,7a*S*,7b*S*)-4,5,7a,7b-(tetramethyl)decahydronaphtho[2,1-*b*]oxiren-4-yl]methyl}isoindolin-1-one (2)



18 **2** (α-/β-epoxide 7:1)

A solution of **18** (45.0 mg, 84 μmol) in dry CH_2Cl_2 (3 mL) was added dropwise to a stirred suspension of *m*-chloroperbenzoic acid (*m*CPBA) (33.3 mg, 0.12 mmol) in CH_2Cl_2 (12 mL) containing $NaHCO_3$ (10.6 mg, 0.13 mmol) at −40 °C under argon, and the mixture was gradually warmed to −5 °C over 3 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ (10 mL) at −5 °C, and the mixture was extracted with EtOAc (3 x 40 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ (3 x 20 mL) and brine (2 x 20 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:2) to give **2** (39.9 mg, 86%) as a colorless viscous liquid. This product proved to exist as a mixture of α-/β-epoxides 7:1 (by 400 MHz ^{1}H NMR), and the mixture could not be separated. $[\alpha]_D^{25}$ +16.9 (*c* 1.28, $CHCl_3$); IR (neat): 2936, 1655, 1592, 1515, 1466, 1436, 1417, 1260, 1239, 1140, 1114, 1027, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (1H, s), 6.81–6.96 (3H, m), 5.34 (7/8H, s), 5.29 (1/8H, s), 4.76 (7/8H, d, *J* = 14.7 Hz), 4.71 (1/8H, d, *J* = 7.2 Hz), 4.62 (1H, d, *J* = 14.7 Hz), 3.85 (3H, s), 3.84 (3H, s), 3.82 (3H, s), 2.87 (1/8H, s), 2.84 (7/8H, d, *J* = 3.8 Hz), 2.76 (1/8H, d, *J* = 14.5 Hz), 2.68 (7/8H, d, *J* = 14.4Hz), 2.64 (7/8H, d, *J* = 14.4 Hz), 2.63 (1/8H, d, *J* = 14.5 Hz), 1.82–1.93 (2H, m), 1.71 (1H, dd, *J* = 12.2, 1.4Hz), 1.57–1.64 (1H, m), 1.47–1.54 (2H, m), 1.20–1.44 (5H, m), 1.25 (3H, s), 1.05 (3H, s), 0.85–0.95 (1H, m), 0.82 (3H, s), 0.78 (3H [7/8], d, *J* = 6.5 Hz,), 0.73 (3H [1/8], d, *J* = 6.5 Hz,); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 160.2, 150.6, 149.2, 148.5, 131.8, 129.8, 129.7, 120.5, 120.4, 119.6, 111.3, 111.1, 97.4, 66.5, 60.8, 55.9, 55.6, 47.4, 46.4, 42.5, 41.2, 39.7, 37.5, 36.3, 34.0, 27.9, 23.6, 18.9, 18.8, 18.1, 17.5, 15.5; HRMS (EI) calcd for $C_{33}H_{43}NO_6$ (M^+), 549.3090, found 549.3039.

(6a*R*,7*S*,9a*S*,11*R*,13a*S*)-2-(3,4-Dimethoxybenzyl)-11-hydroxy-5-methoxy-6a,7,10,10-tetramethyl-2,3,6,6a,7,8,9,9a,10,11,12,13-dodecahydro-1*H*-benzo[8,8a][1]benzopyrano[2,3-*e*]isoindol-3-one (19a) and its (6a*R*,7*S*,9a*S*,11*S*,13a*S*)-isomer (19b)



2 (α-/β-epoxide 7:1) **19a** (66%) **19b** (9%)

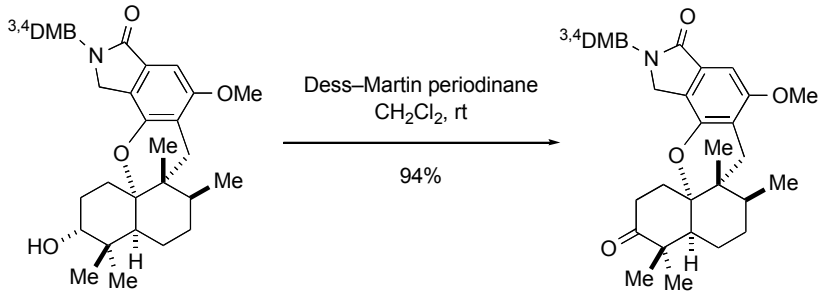
A solution of $BF_3{\cdot}Et_2O$ (84.5 μL, 0.64 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise to a stirred solution of **2** (α-/β-epoxide 7:1) (35.2 mg, 64 μmol) in dry CH_2Cl_2 (6 mL) at −40 °C under argon, and the mixture was allowed to warm to room temperature over 2 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL), and the resulting mixture was extracted with CH_2Cl_2 (3 x 30 mL). The combined extracts were washed with brine (2 x 20 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (benzene/EtOAc 1:1) to give **19a** (23.2 mg, 66%, more polar) and **19b** (3.1 mg, 9%, less polar).

Compound 19a: white amorphous powder; $[\alpha]_D^{27}$ −33.1 (*c* 1.02, $CHCl_3$); IR (KBr): 3316, 2938, 1667, 1606, 1514, 1472, 1438, 1414, 1317, 1260, 1106, 1026, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.93 (1H, s), 6.80 (3H, m), 5.00 (1H, d, *J* = 14.8 Hz), 4.43 (1H, d, *J* = 14.8 Hz), 4.18 (2H, d, *J* = 3.2 Hz), 3.88 (3H, s), 3.87 (3H, s), 3.84 (3H, s), 3.12 (1H, d, *J* = 18.0 Hz), 2.21 (1H, d, *J* = 18.0 Hz), 1.98–2.13 (3H, m), 1.85–1.90 (1H, m), 1.75–1.84 (3H, m), 1.63–1.72 (2H, m), 1.55 (1H, dd, *J* = 13.6, 4.2 Hz), 1.39 (1H, d, *J* = 14.3 Hz), 1.24–1.32 (1H, m), 1.12 (3H, d, *J* = 7.5 Hz), 0.97 (3H, s), 0.95 (3H, s), 0.84 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 158.4, 149.3, 148.5, 147.1, 131.9, 130.0, 120.9, 120.5, 113.5, 111.3, 111.1, 96.0, 83.0, 73.9, 56.0, 55.9, 55.8, 47.6, 47.0, 46.3, 39.3, 38.4, 37.4, 32.6, 29.5, 27.9, 27.8, 27.2, 23.2, 22.3, 20.2, 17.2; HRMS (EI) calcd for $C_{33}H_{43}NO_6$ (M^+), 549.3090, found 549.3089.

Compound 19b: colorless viscous liquid; $[\alpha]_D^{25}$ +71.7 (*c* 2.82, $CHCl_3$); IR (neat): 2958, 2935, 1672, 1624, 1604, 1515, 1471, 1462, 1436, 1368, 1259, 1119, 974, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.85 (1H, s), 6.73–6.78 (3H, m), 4.89 (1H, d, *J* = 14.6 Hz), 4.41 (1H, d, *J* = 14.6 Hz), 4.01–4.12 (1H, m), 4.08 (1H, d, *J* = 8.8 Hz), 3.81 (3H, s), 3.79 (3H, s), 3.76 (3H, s), 3.45 (1H, s), 3.09 (1H, d, *J* = 18.0 Hz), 2.30–2.33 (1H, m),

2.18–2.21 (1H, m), 2.14 (1H, d, J = 18.0 Hz), 1.48–1.69 (7H, m), 1.17–1.28 (4H, m), 1.06 (3H, d, J = 7.8 Hz), 0.88 (3H, s), 0.87 (3H, s), 0.80 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 158.4, 149.3, 148.5, 147.1, 131.6, 130.0, 120.8, 120.3, 113.8, 111.2, 111.1, 95.8, 83.8, 74.5, 55.9, 55.8, 55.7, 47.5, 46.3, 44.6, 39.5, 37.9, 37.6, 32.2, 31.5, 30.2, 28.0, 25.8, 24.1, 23.7, 20.2, 17.1; HRMS (EI) calcd for $C_{33}H_{43}NO_6$, 549.3090 (M^+), found 549.3090.

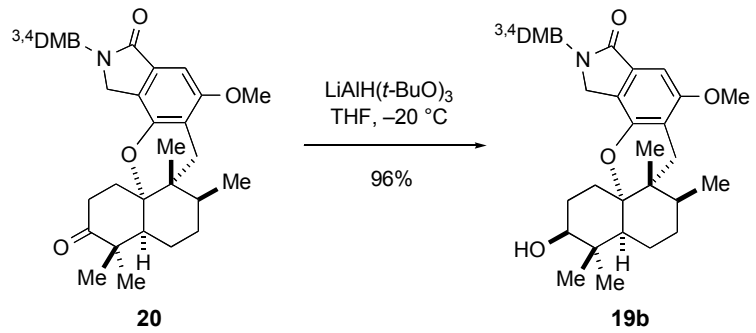
(6a*R*,7*S*,9a*S*,11*R*,13a*S*)-2-(3,4-Dimethoxybenzyl)-5-methoxy-6a,7,10,10-tetramethyl-2,3,6,6a,7,8,9,9a,10,11,12,13-dodecahydro-1*H*-benzo[8,8a][1]benzopyrano[2,3-*e*]isoindol-3,11-dione (20)



19a **20**

Dess–Martin periodinane (62.0 mg, 0.14 mmol) was added in small portions to a stirred solution of **19a** (40.0 mg, 72 μmol) in CH_2Cl_2 (10 mL) at room temperature. After 1 h, the reaction was quenched with saturated aqueous $Na_2S_2O_3$ (6 mL), and the mixture was extracted with EtOAc (3 x 30 mL). The combined extracts were washed with brine (2 x 20 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography (hexane/EtOAc 1:1) to give **20** (37.4 mg, 94%) as a colorless viscous liquid. $[\alpha]_D^{25}$ +68.8° (c 3.76, $CHCl_3$); IR (neat): 2963, 2933, 1684, 1625, 1604, 1514, 1472, 1436, 1259, 1118, 1027, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 (1H, s), 6.80 (3H, dd, J = 17.0, 7.8 Hz), 4.99 (1H, d, J = 14.6 Hz), 4.40 (1H, d, J = 14.6 Hz), 4.06–4.18 (1H, m), 4.14 (1H, d, J = 8.8 Hz), 3.86 (3H, s), 3.83 (3H, s), 3.81 (3H, s), 3.07 (1H, d, J = 18.0 Hz), 2.92–3.00 (1H, m), 2.33–2.45 (2H, m), 2.21–2.28 (1H, m), 2.26 (1H, d, J = 18.0 Hz), 2.14 (1H, dd, J = 14.1, 7.8 Hz), 2.01–2.06 (1H, m), 1.96 (1H, d, J = 11.7 Hz), 1.80 (2H, d, J = 7.3 Hz), 1.31–1.41 (2H, m), 1.10 (3H, s), 1.07 (2H, d, J = 7.8 Hz), 0.94 (3H, s), 0.88 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 158.5, 149.2, 148.5, 146.6, 132.1, 129.8, 120.9, 120.4, 113.5, 111.3, 111.1, 96.5, 82.2, 55.9, 55.8 (2 C), 55.7, 48.5, 47.7, 47.3, 46.3, 38.8, 37.3, 33.4, 32.5, 30.1, 29.0, 27.7, 24.2, 23.9, 20.3, 17.2; HRMS (EI) calcd for $C_{33}H_{41}NO_6$ (M^+), 547.2933, found 547.2939.

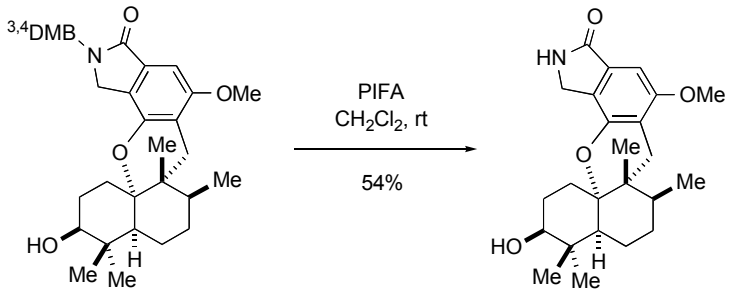
Conversion of compound 20 to compound 19b by stereoselective reduction



20 **19b**

$LiAlH(t\text{-}BuO)_3$ (81.3 mg, 0.32 mmol) in dry THF (2 mL) was added dropwise to a stirred solution of **20** (35.0 mg, 64 μmol) in dry THF (5 mL) at −20 °C. After 3 h, the reaction was quenched with 1 M HCl (5 mL), and the resulting mixture was extracted with EtOAc (3 x 30 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ (2 x 20 mL) and brine (2 x 20 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography ($CHCl_3$/MeOH 30:1) to give **19b** (33.7 mg, 96%) as a colorless viscous liquid. The IR, ^1H and ^{13}C NMR, MS spectra of this sample was identical with those recorded for **19b**.

(6a*R*,7*S*,9a*S*,11*S*,13a*S*)-11-Hydroxy-5-methoxy-6a,7,10,10-tetramethyl-2,3,6,6a,7,8,9,9a,10,11,12,13-dodecahydro-1*H*-benzo[8,8a][1]benzopyrano[2,3-*e*]isoindol-3-one (21)

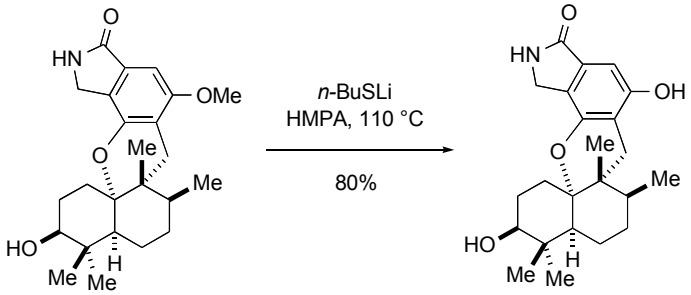


19b **21**

[Bis(trifluoroacetoxy)iodo]benzene (PIFA) (160 mg, 0.36 mmol) was added to a stirred solution of **19b** (20.0 mg, 36 μmol) in dry CH_2Cl_2 (5 mL) at room temperature. After 4 h, the reaction was quenched with 10% aqueous $Na_2S_2O_3$ (10 mL) at room temperature, and the mixture was extracted with $CHCl_3$ (3 x 30 mL). The combined extracts were washed with brine (2 x 20 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography ($CHCl_3$/MeOH 20:1) to

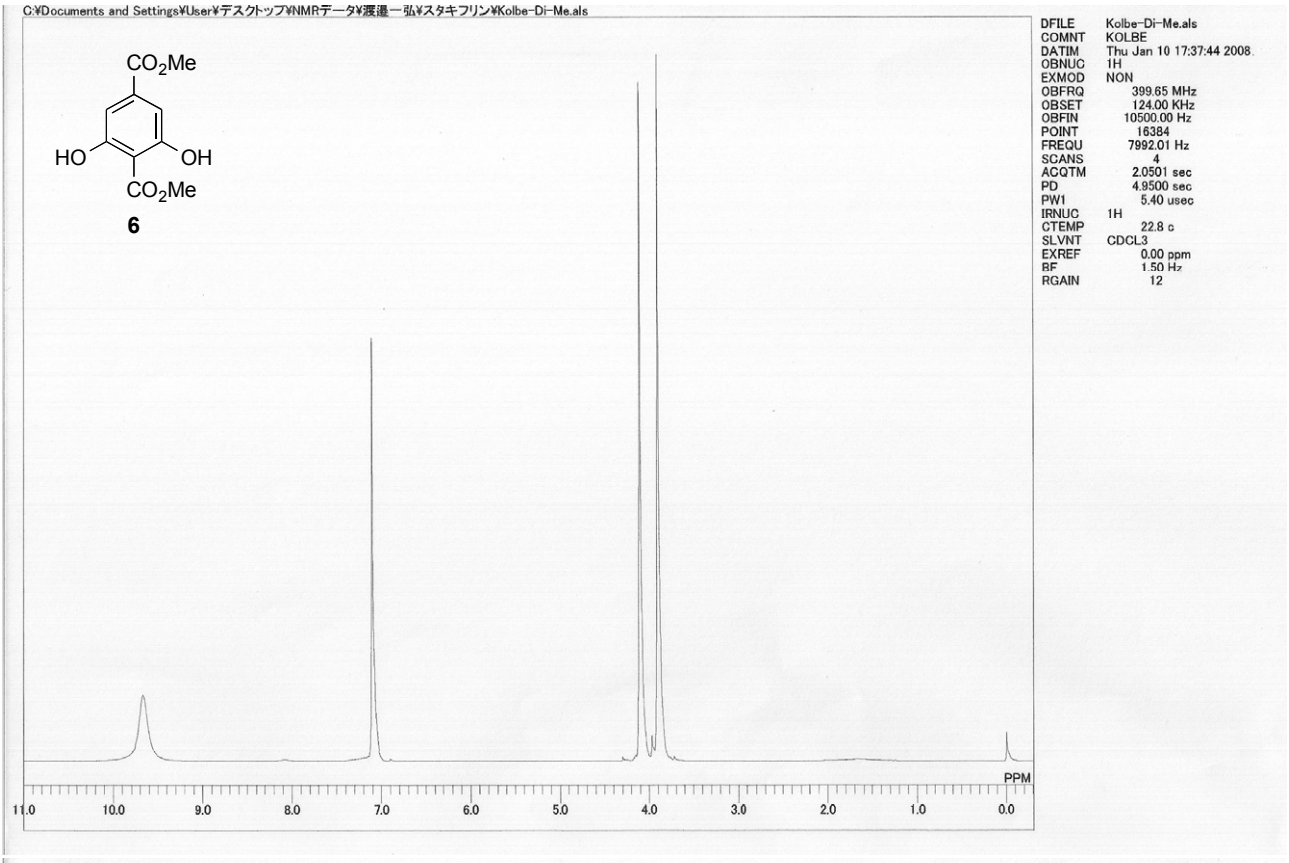
give **21** (7.8 mg, 54%) as a white amorphous powder. $[\alpha]_D^{24}$ +85.8 (*c* 0.62, $CHCl_3$); IR (KBr): 3415, 2961, 1681, 1624, 1602, 1471, 1433, 1367, 1353, 1172, 1120, 1102, 973, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.82 (1H, s), 6.51(1H, s), 4.28 (2H, d, *J* = 4.4 Hz), 3.81 (3H, s), 3.49 (1H, s), 3.12 (1H, d, *J* = 18.0 Hz), 2.37–2.43 (1H, m), 2.18–2.27 (1H, m), 2.17 (1H, d, *J* = 18.0 Hz), 1.91–2.07 (3H, m), 1.59–1.81 (6H, m), 1.52 (1H, d, *J* = 12.6 Hz), 1.29 (1H, d, *J* = 13.6 Hz), 1.09 (2H, d, *J* = 7.8 Hz), 0.93 (3H, s), 0.91 (3H, s), 0.84 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 147.3, 130.7, 123.3, 114.4, 95.6, 83.9, 74.6, 55.8, 44.7, 39.6, 37.9, 37.6, 32.2, 30.3, 28.1, 26.4, 25.8, 24.1, 23.8, 23.7, 20.2, 17.1, 14.2; HRMS (EI) calcd for $C_{24}H_{33}NO_4$ (M^+), 399.2409, found 399.2397.

(6a*R*,7*S*,9a*S*,11*S*,13a*S*)-5,11-Dihydroxy-5-methoxy-6a,7,10,10-tetramethyl-2,3,6,6a,7,8,9,9a,10,11,12,13-dodecahydro-1*H*-benzo[8,8a][1]benzopyrano[2,3-*e*]isoindol-3-one [(+)-stachyflin] (1)



Lithium *n*-butylthiolate (*n*-BuSLi) in hexamethylphosphorous triamide (HMPA) (0.5 M solution, 0.90 mL, 0.45 mmol) was added to a stirred solution of **21** (6.0 mg, 15 μmol) in dry HMPA (0.3 mL) at room temperature, and the mixture was heated at 110 °C for 4 h. After cooling, the reaction was quenched with saturated aqueous NH_4Cl (1 mL), and the resulting mixture was extracted with $CHCl_3$ (3 x 20 mL). The combined extracts were washed with brine (3 x 10 mL), then dried over Na_2SO_4. Concentration of the solvent in vacuo afforded a residue, which was purified by column chromatography ($CHCl_3$/MeOH 20:1→10:1) to give **1** (4.6 mg, 80%) as a white solid. Recrystallization from $CHCl_3$/MeOH 10:1 afforded colorless needles, mp >300 °C (lit.[2b] mp >300 °C); $[\alpha]_D^{24}$ +133.3 (*c* 0.46, MeOH) {lit.[2b] $[\alpha]_D^{24}$ +138.7 (*c* 1.00, MeOH)}. The IR, ^1H and ^{13}C NMR, and MS spectra (see below) were identical to those of natural (+)-stachyflin. IR (KBr) 3316, 2938, 1667, 1606, 1514, 1472, 1438, 1414, 1317, 1260, 1106, 1026, 755 cm^{-1}; ^1H NMR (400 MHz, DMSO-*d*6): δ 9.78 (1H, s), 8.33 (1H, s), 4.49 (1H, s), 4.20 (1H, d, *J* = 17.1 Hz), 4.09 (1H, d, *J* = 17.1 Hz), 3.22–3.43 (4H, m), 3.11 (1H, d, *J* = 17.6 Hz), 2.23 (1H, t, *J* = 13.6 Hz), 1.96–2.33 (4H, m), 1.79 (1H, t, *J* = 6.3 Hz), 1.71 (1H, d, *J* = 12.2 Hz), 1.61 (2H, t, *J* = 13.1 Hz), 1.54 (1H, d, *J* = 9.8

Hz), 1.23 (1H, d, J = 7.3 Hz), 1.16 (1H, d, J = 7.8 Hz), 0.98 (3H, s), 0.95 (3H, s), 0.89 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 155.9, 147.2, 131.6, 120.8, 112.0, 99.0, 83.3, 72.2, 44.4, 42.5, 37.4, 37.1, 31.9, 31.3, 30.1, 27.6, 27.0, 25.7, 23.5, 23.4, 19.9, 16.8; HRMS (EI) calcd for $C_{23}H_{31}NO_4$, 385.2253 (M^+), found 385.2250.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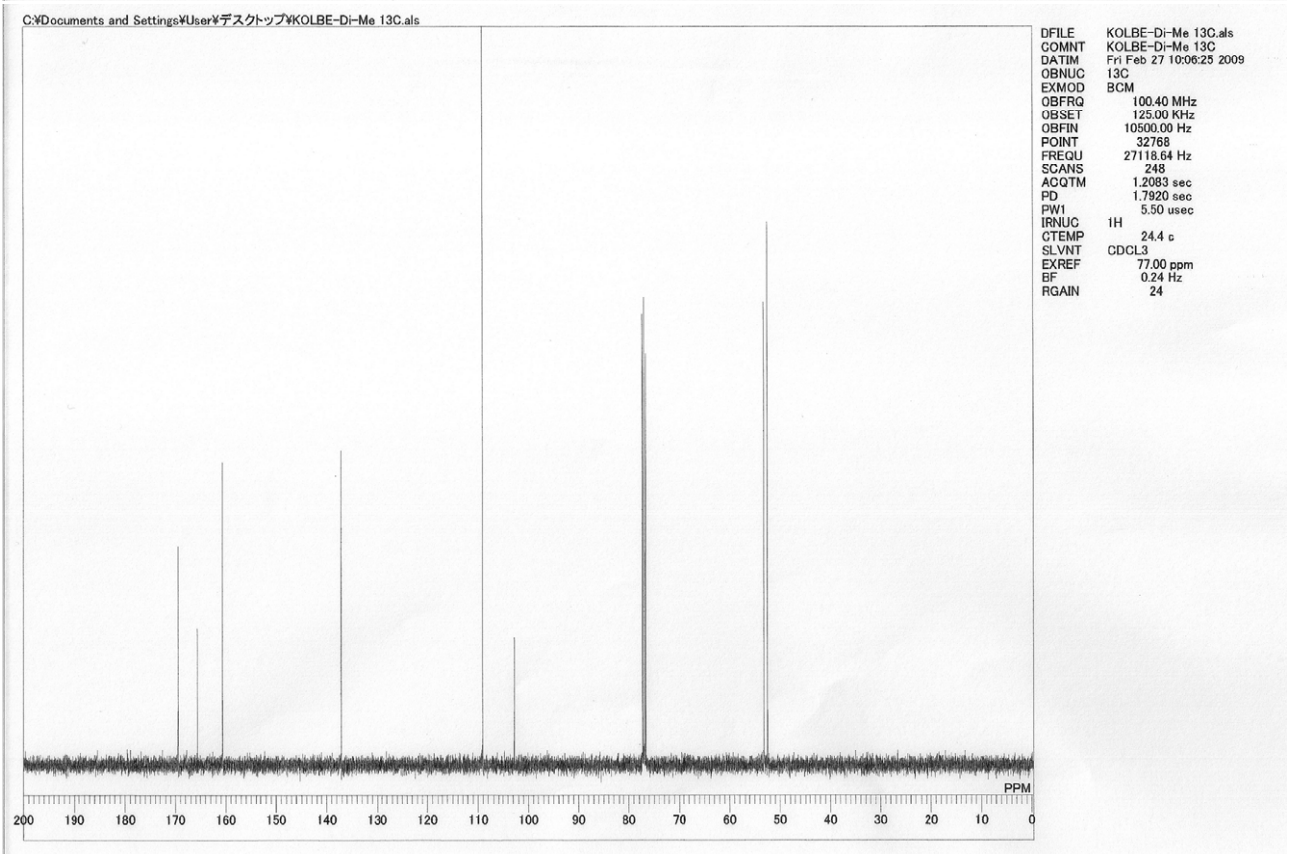
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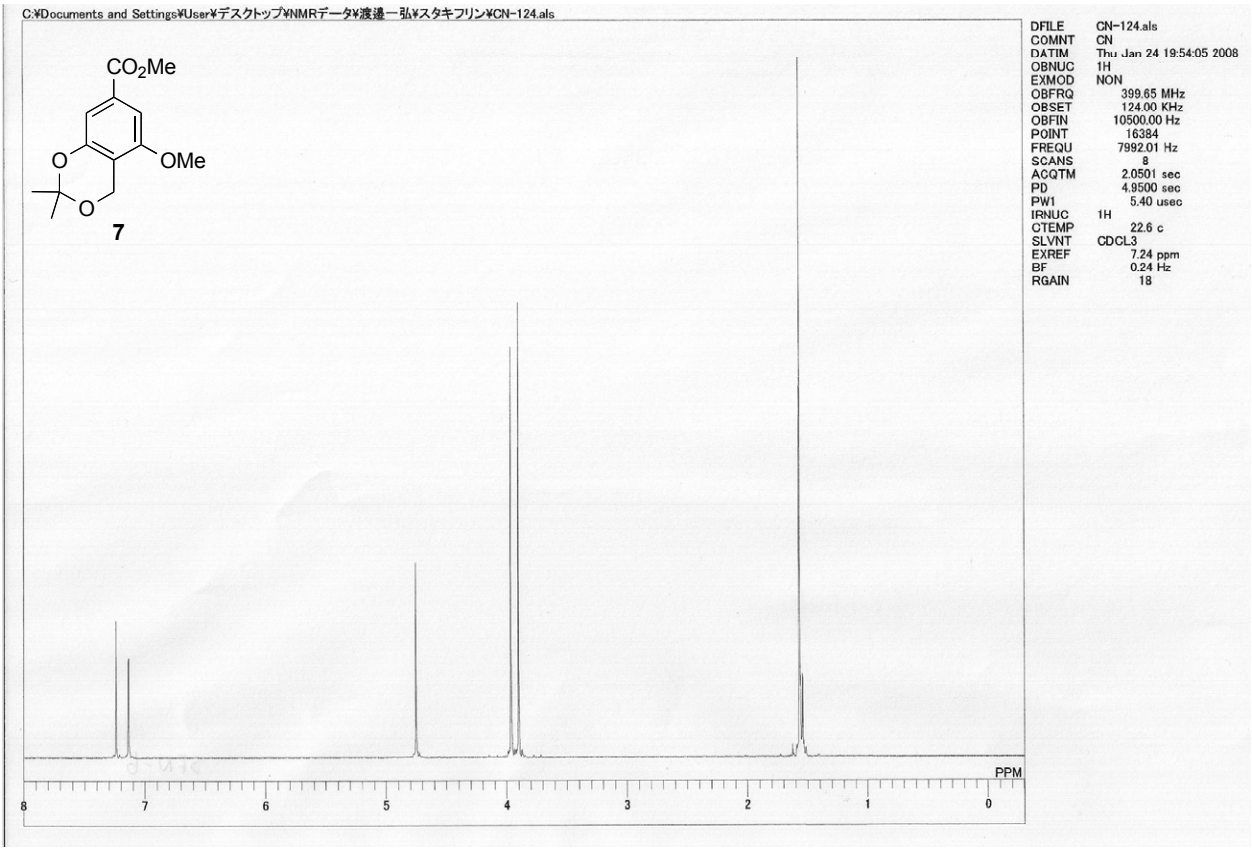
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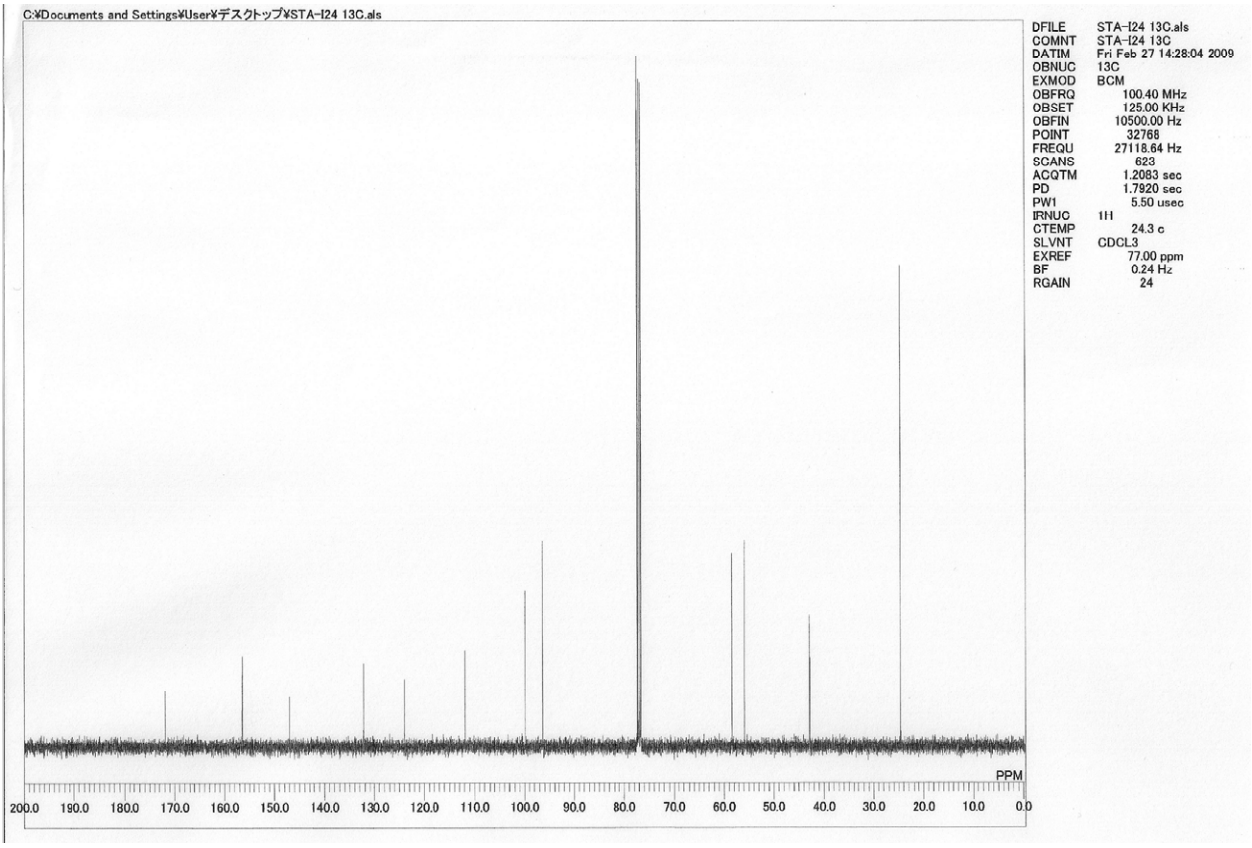
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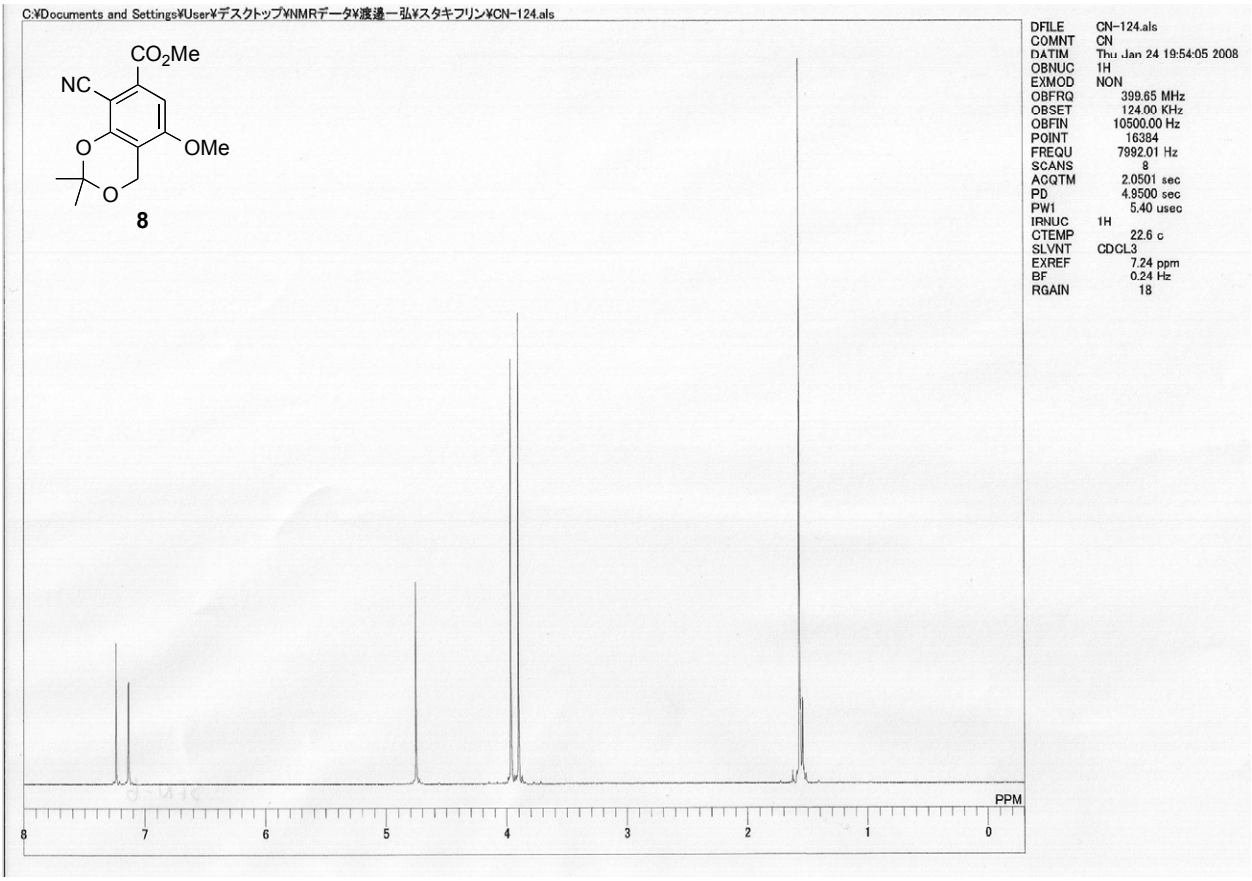
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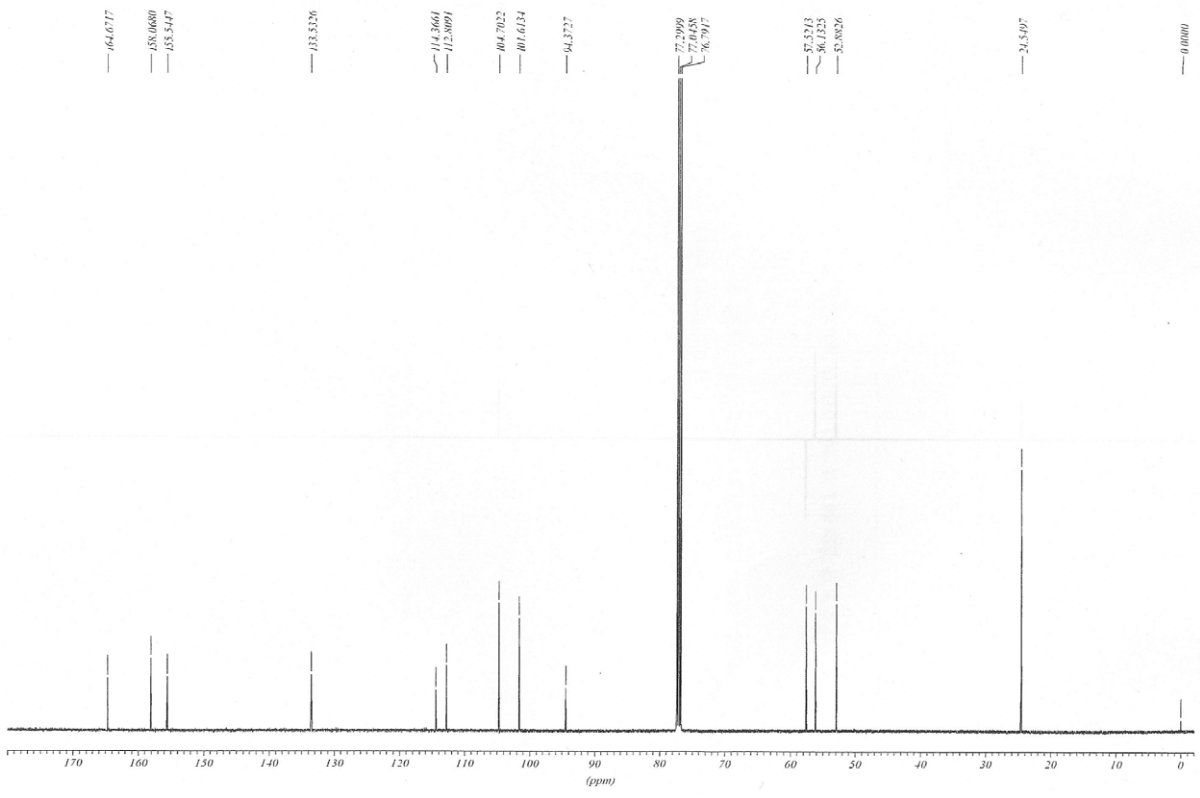
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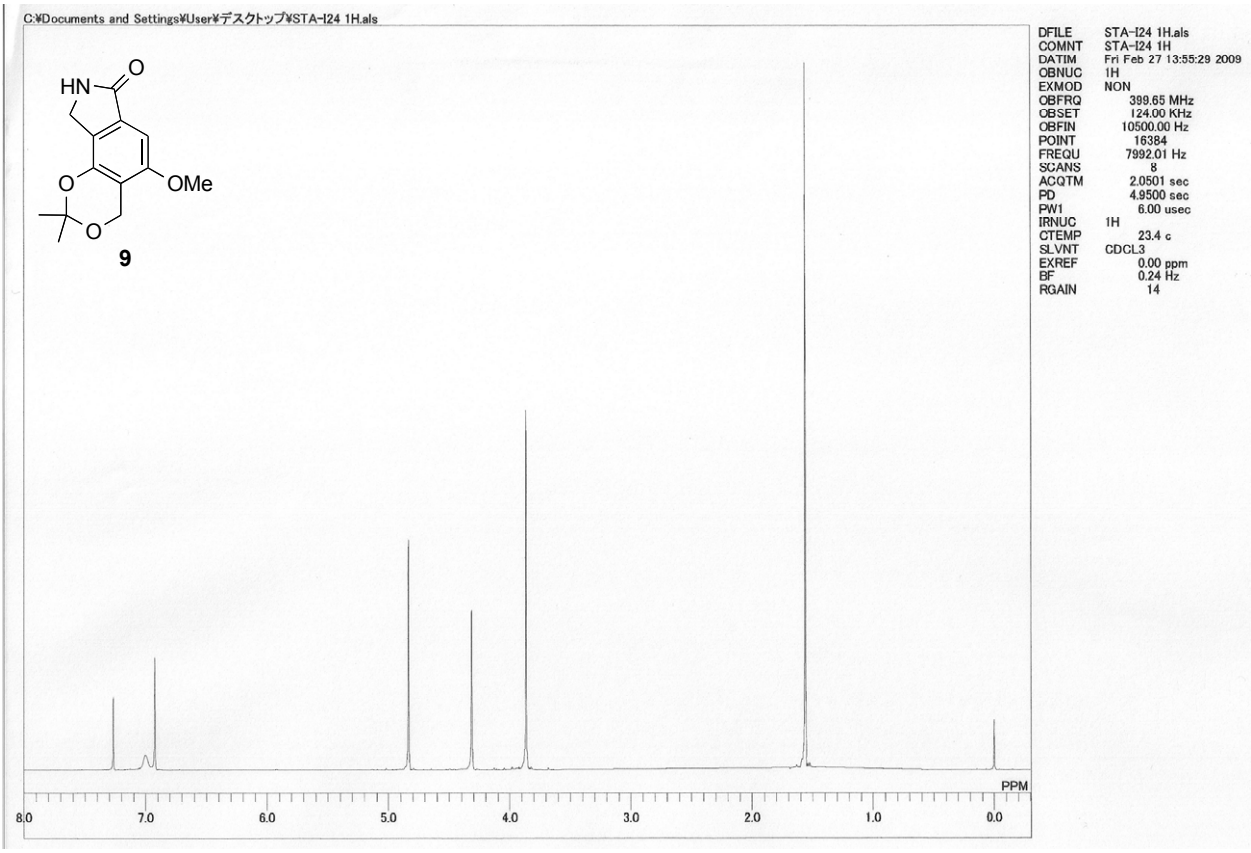
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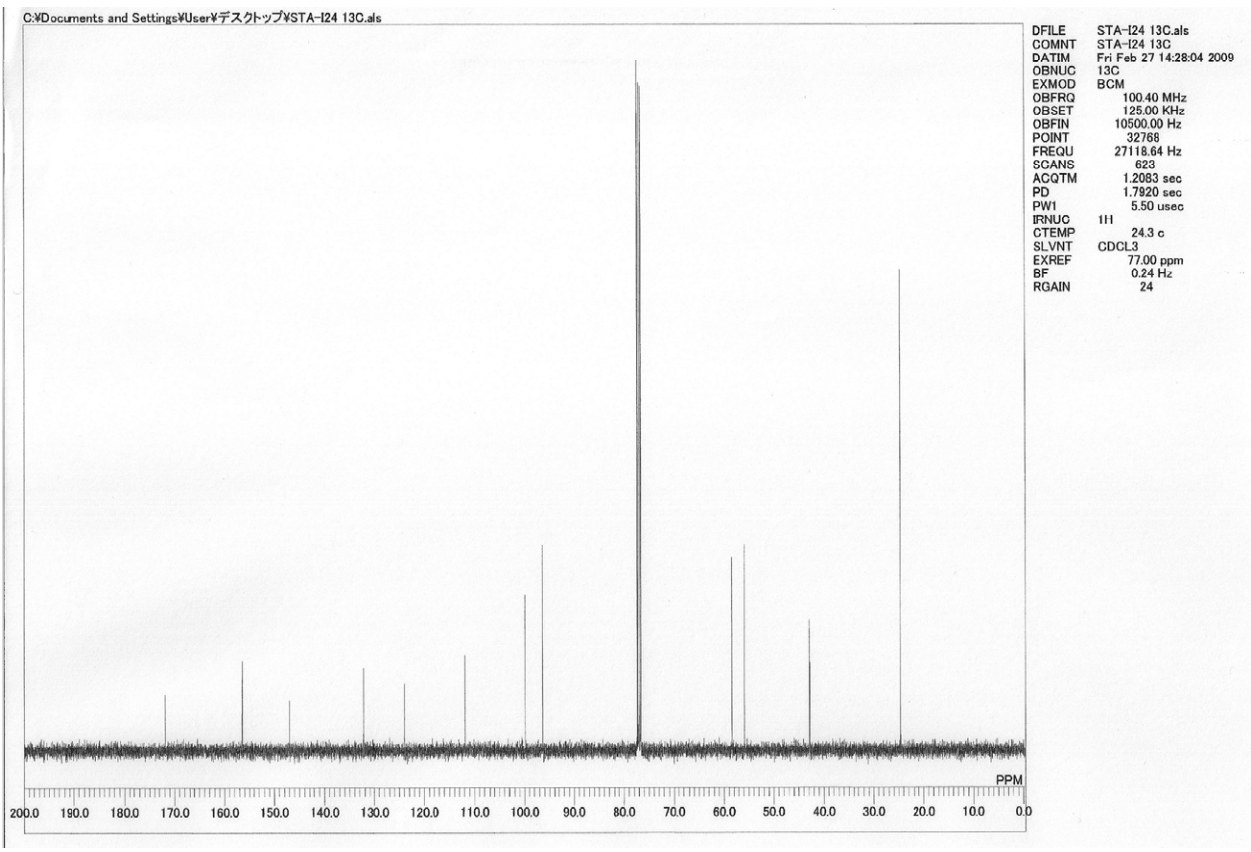
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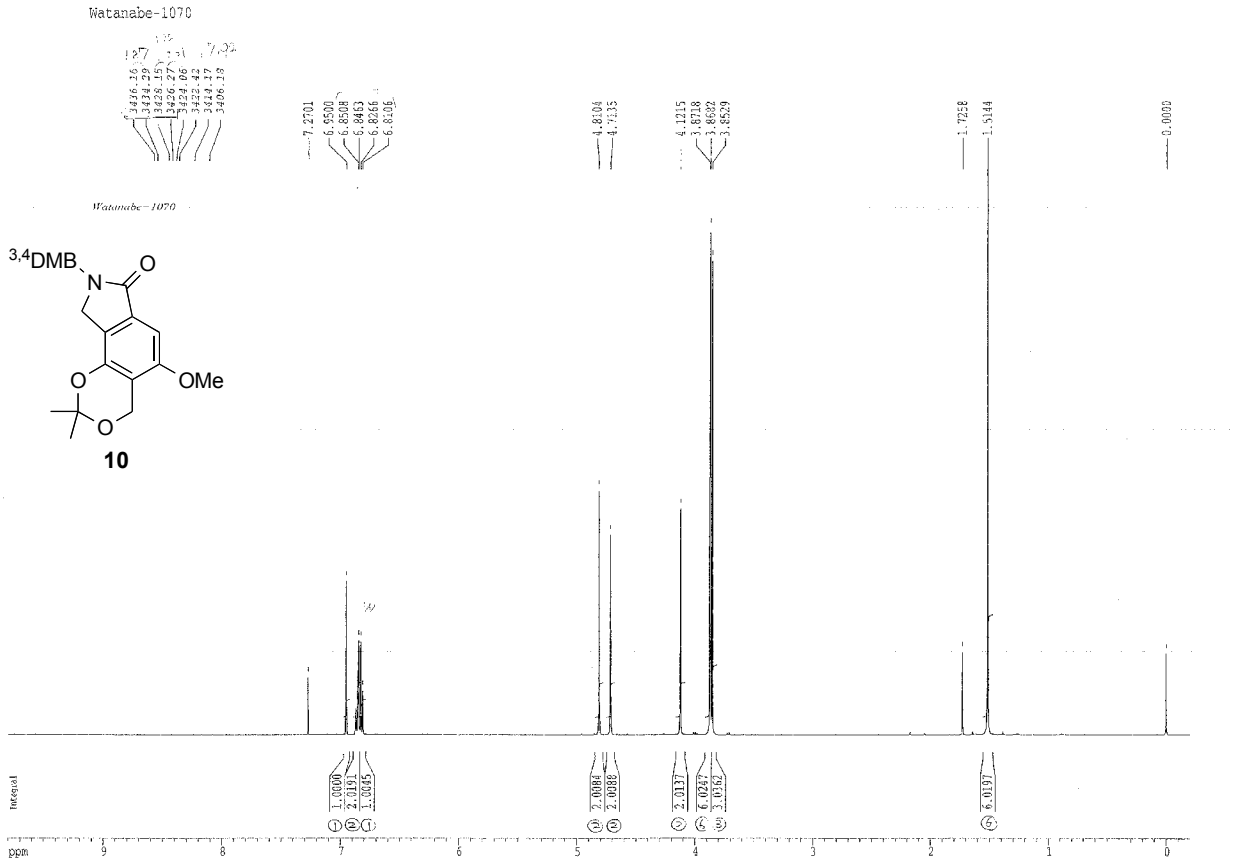
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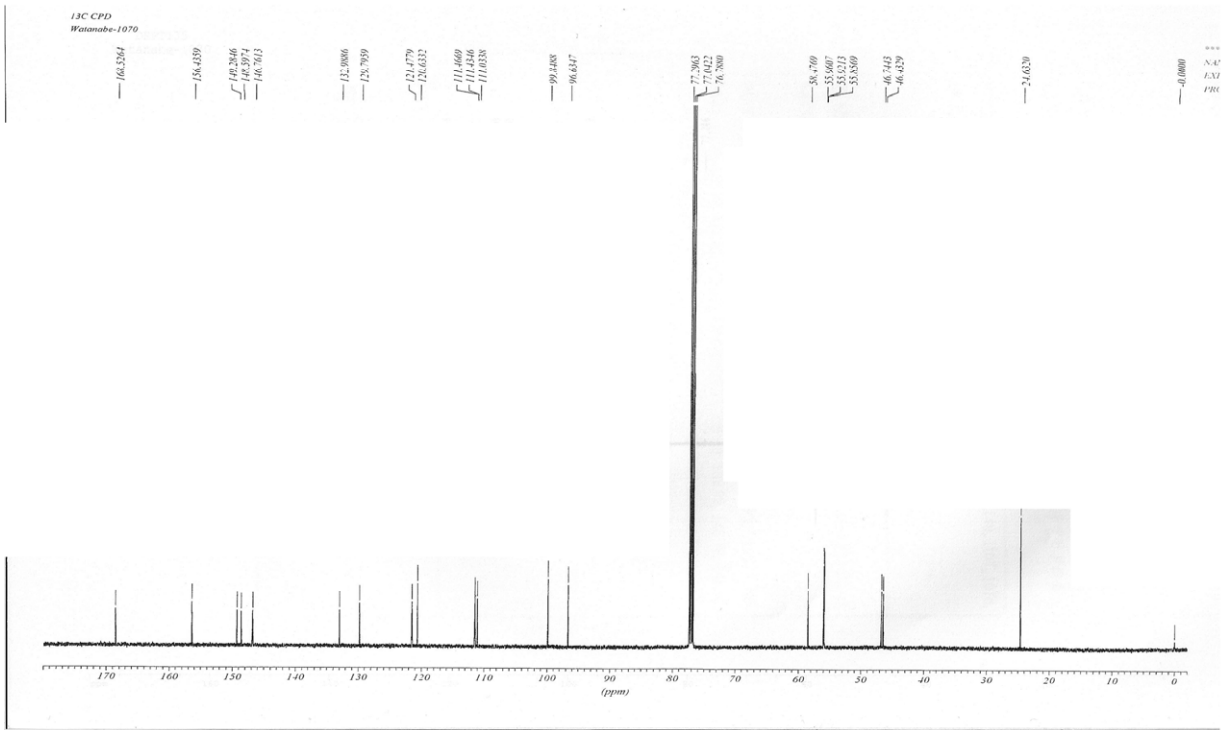
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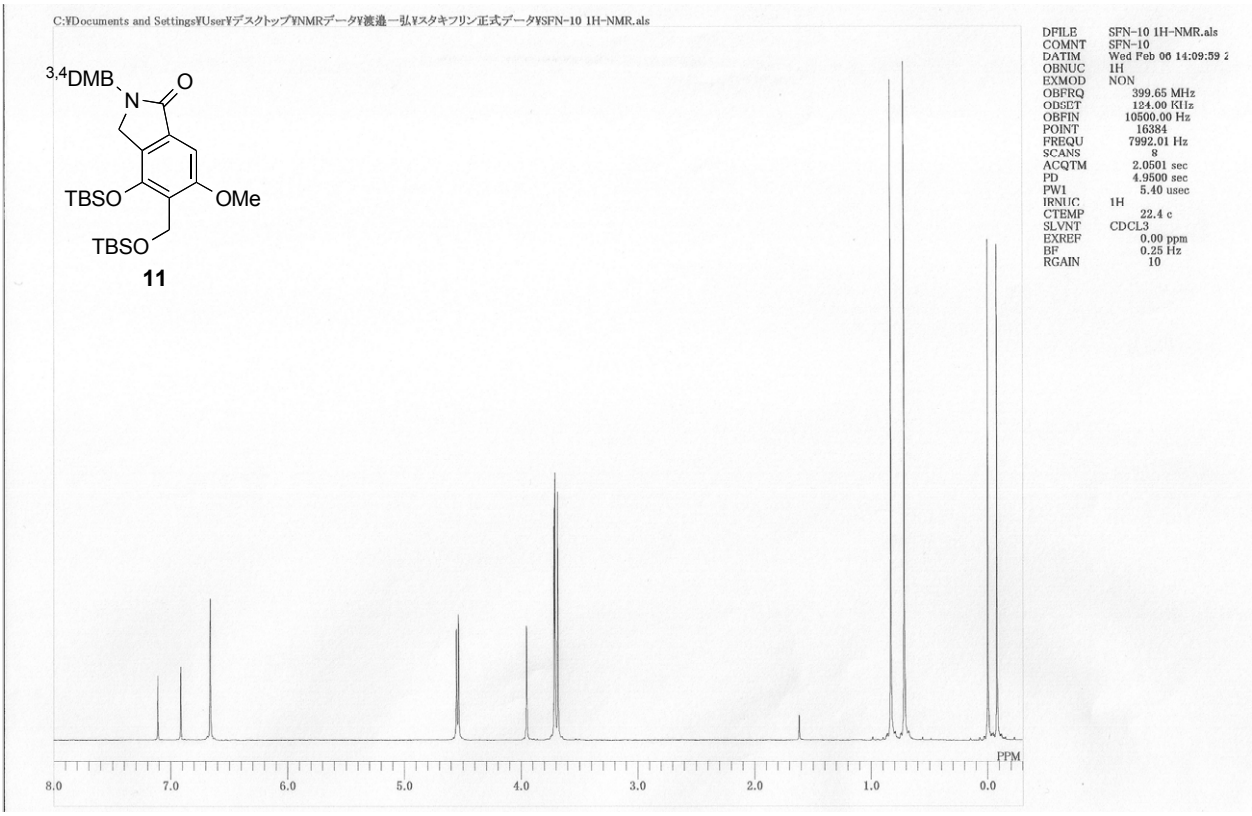
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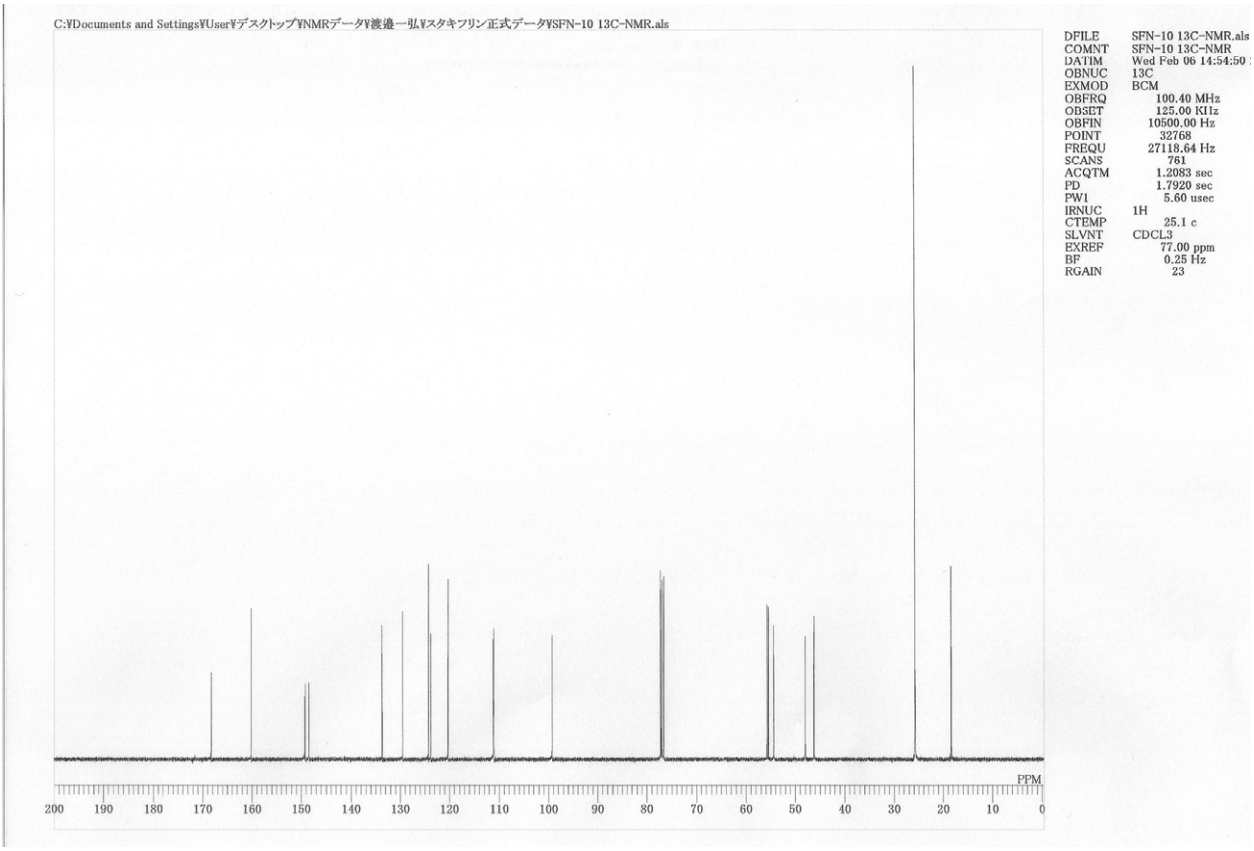
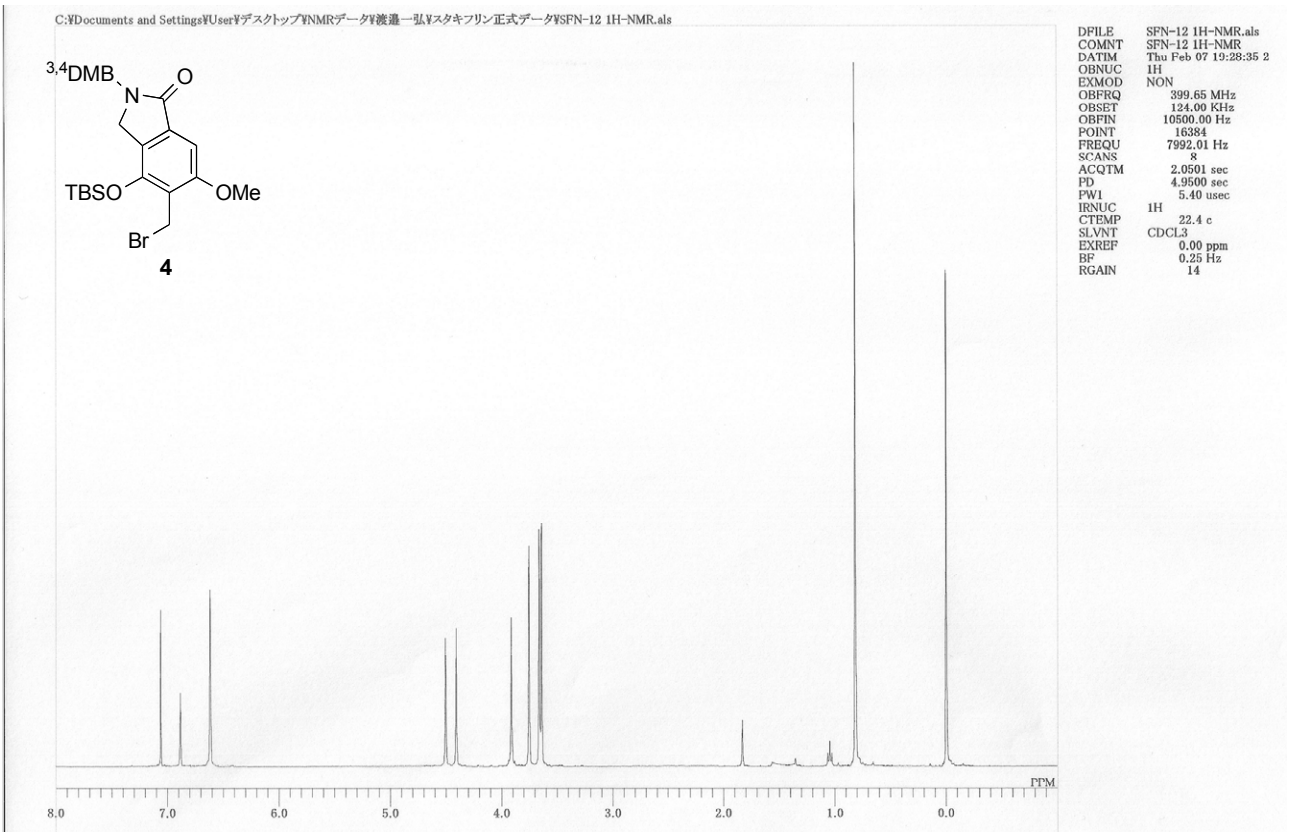
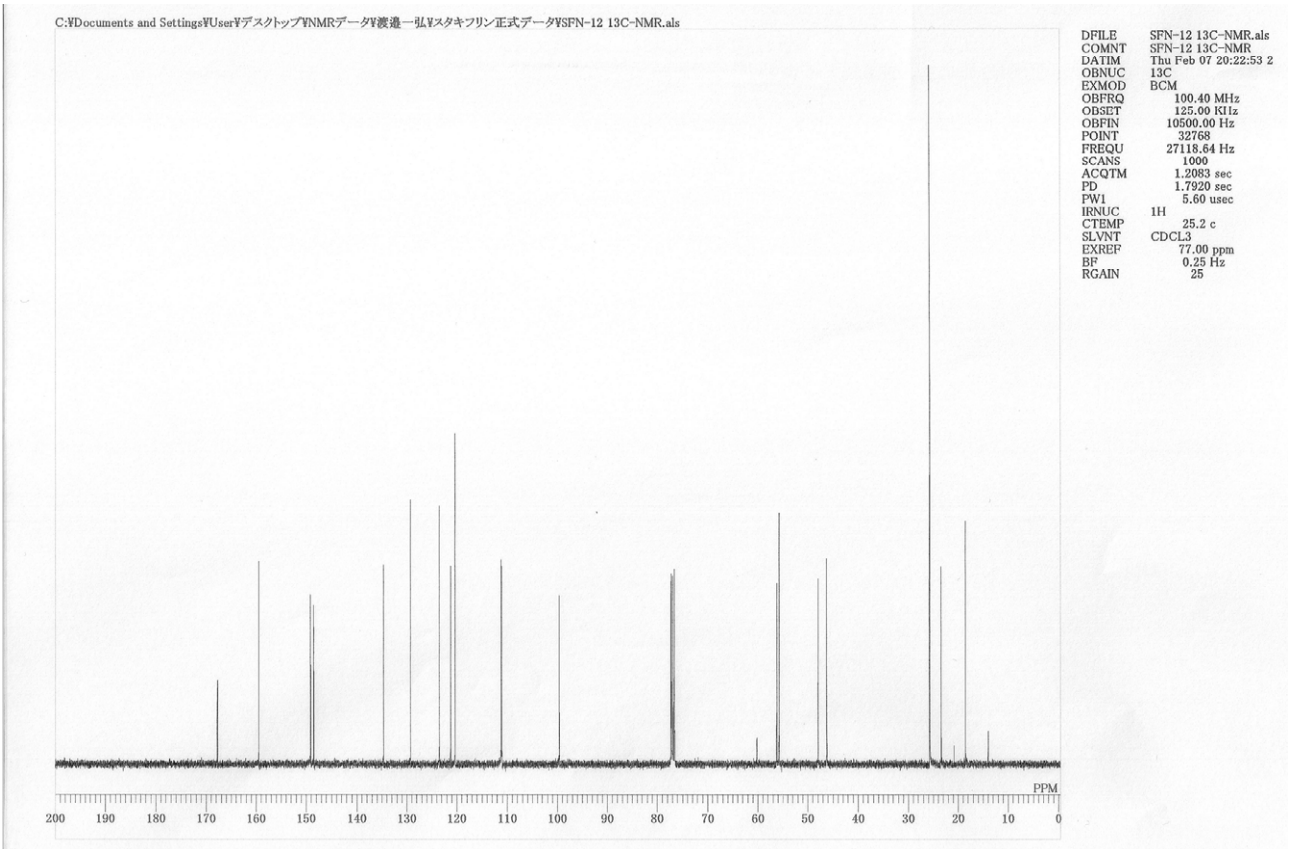
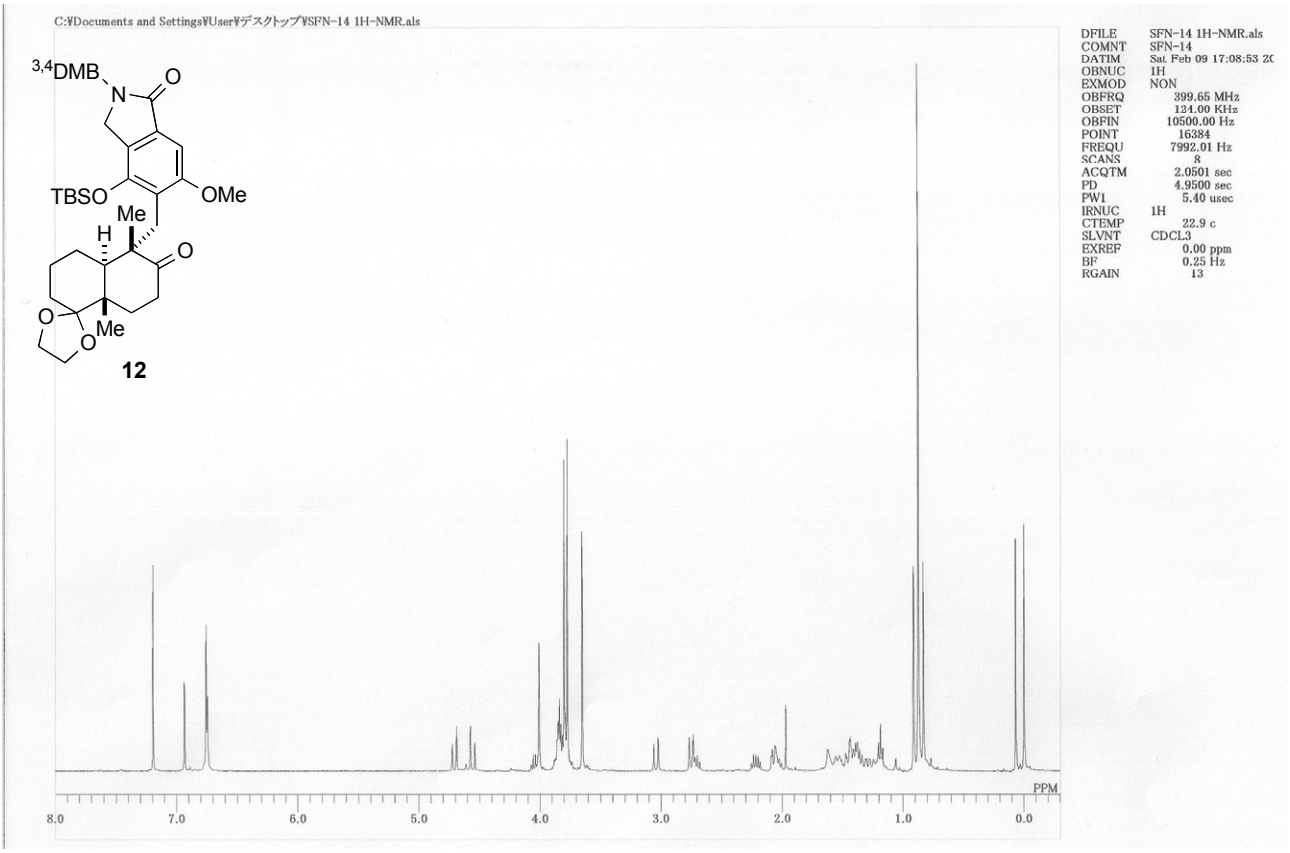
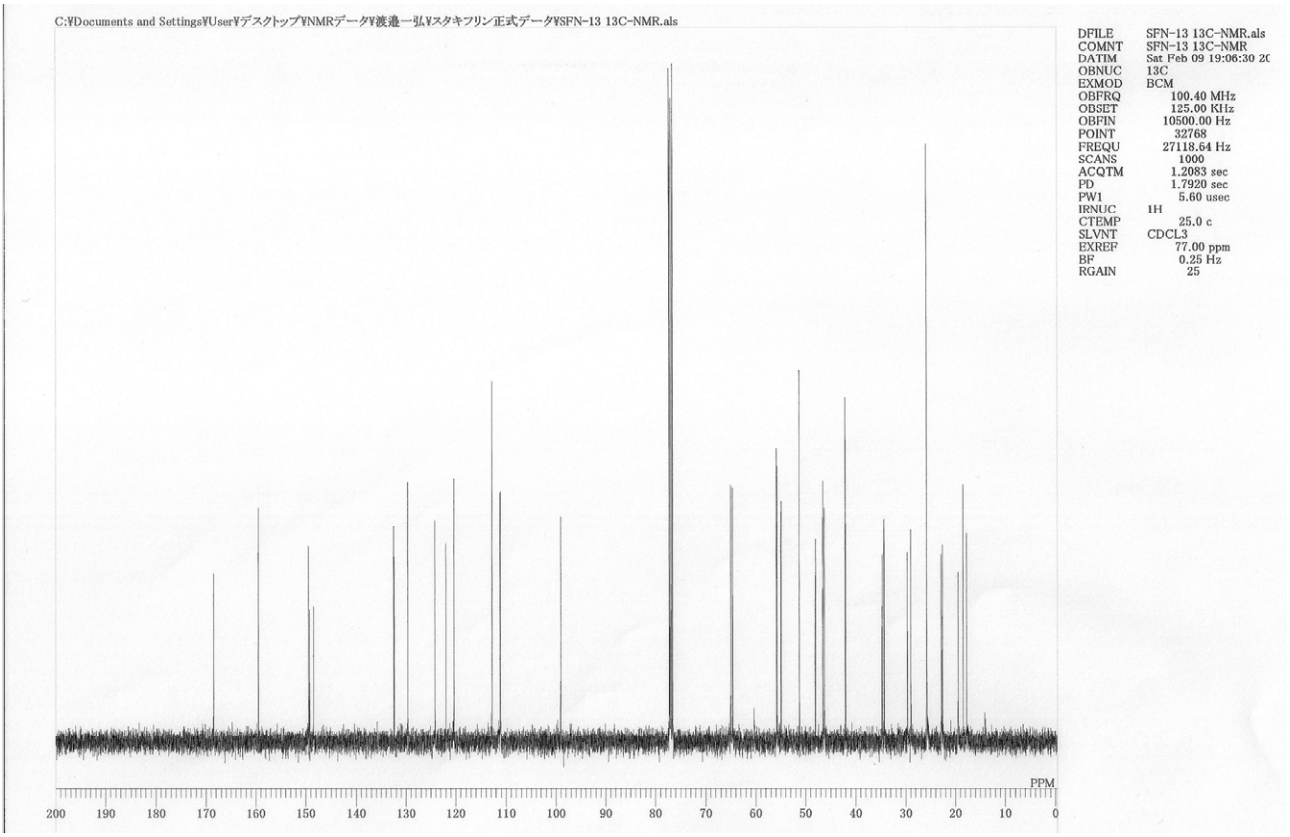
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.25 Hz
RGAIN 10
PPM
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

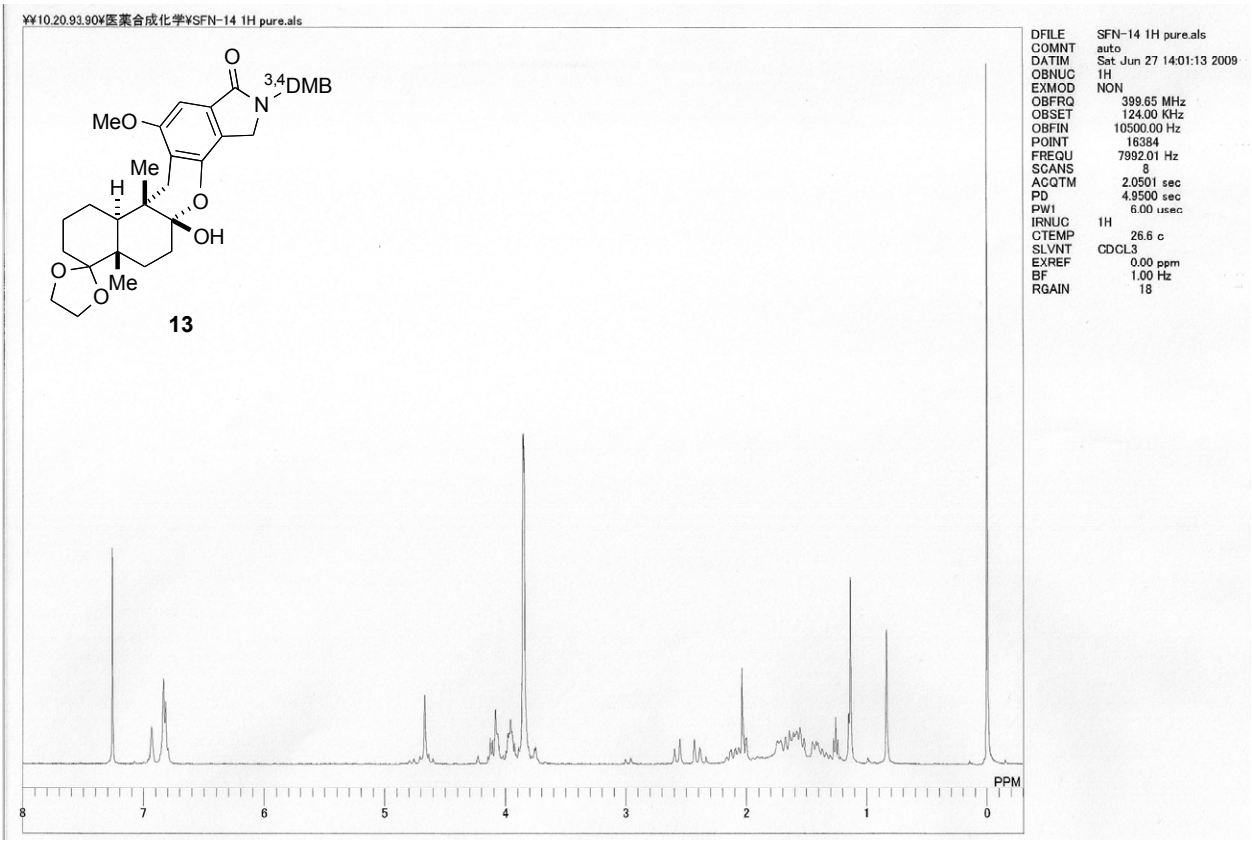

C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-10 13C-NMR.als
DFILE SFN-10 13C-NMR.als
COMNT SFN-10 13C-NMR
DATIM Wed Feb 06 14:54:50
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 761
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 25.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.25 Hz
RGAIN 23
PPM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

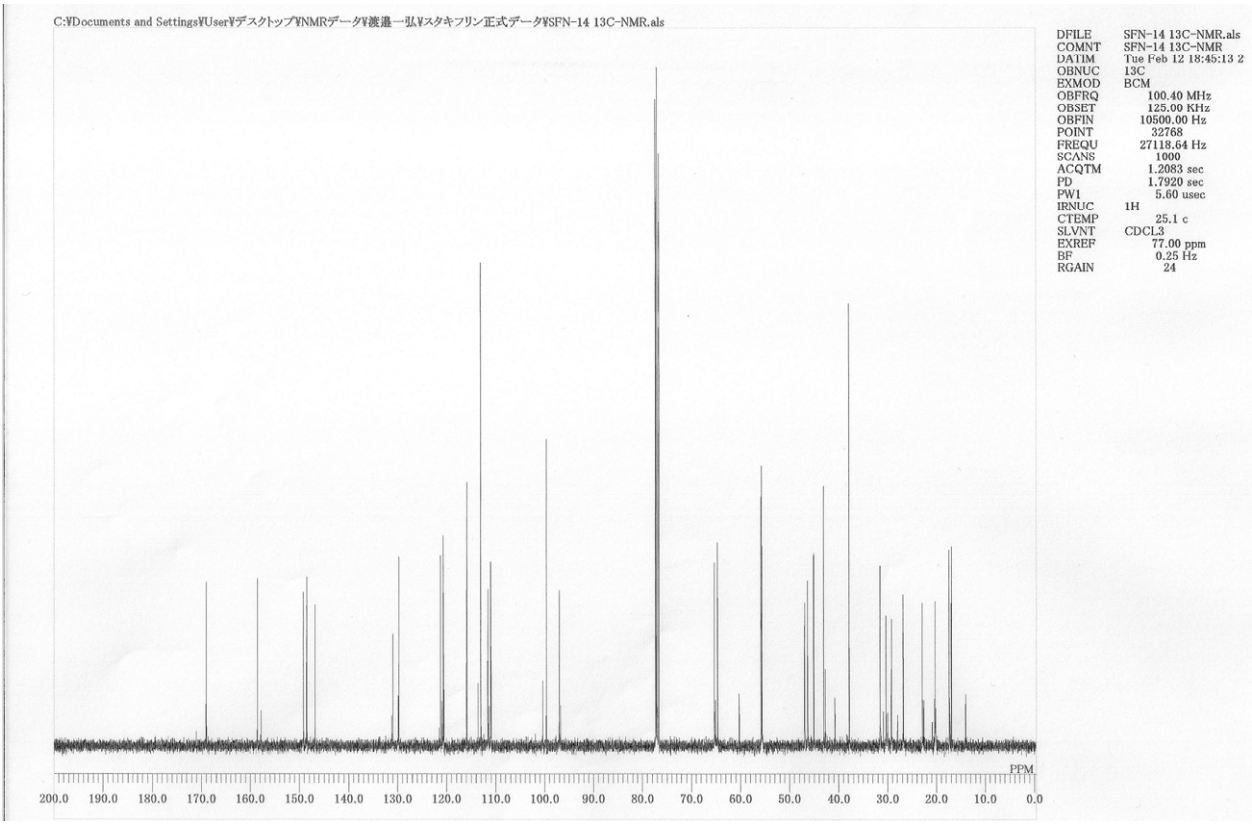

C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-12 1H-NMR.als
3,4DMB
N
O
TBSO
OMe
Br
4
DFILE SFN-12 1H-NMR.als
COMNT SFN-12 1H-NMR
DATIM Thu Feb 07 19:28:35 2
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.25 Hz
RGAIN 14
PPM
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

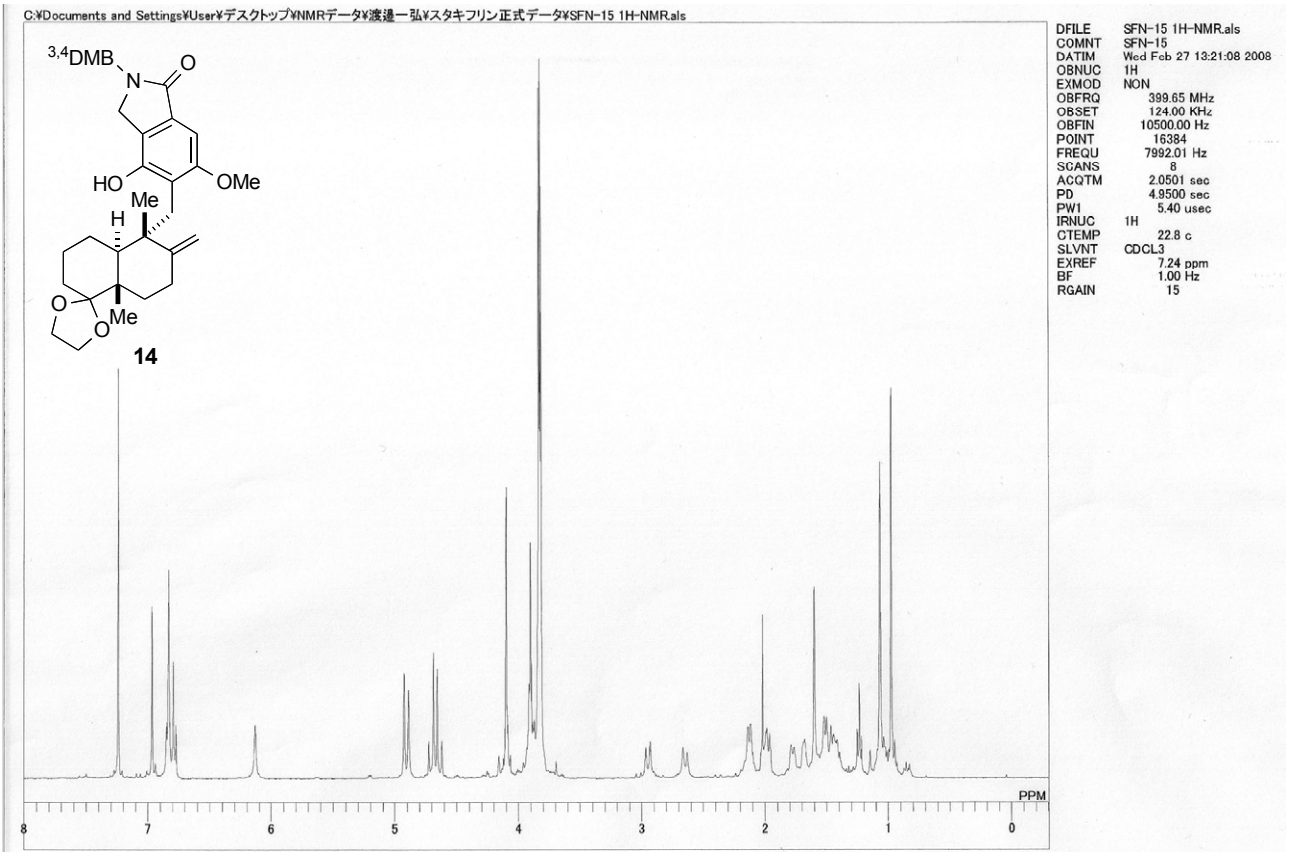

C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-12 13C-NMR.als
DFILE SFN-12 13C-NMR.als
COMNT SFN-12 13C-NMR
DATIM Thu Feb 07 20:22:53 2
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 1000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 25.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.25 Hz
RGAIN 25
PPM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

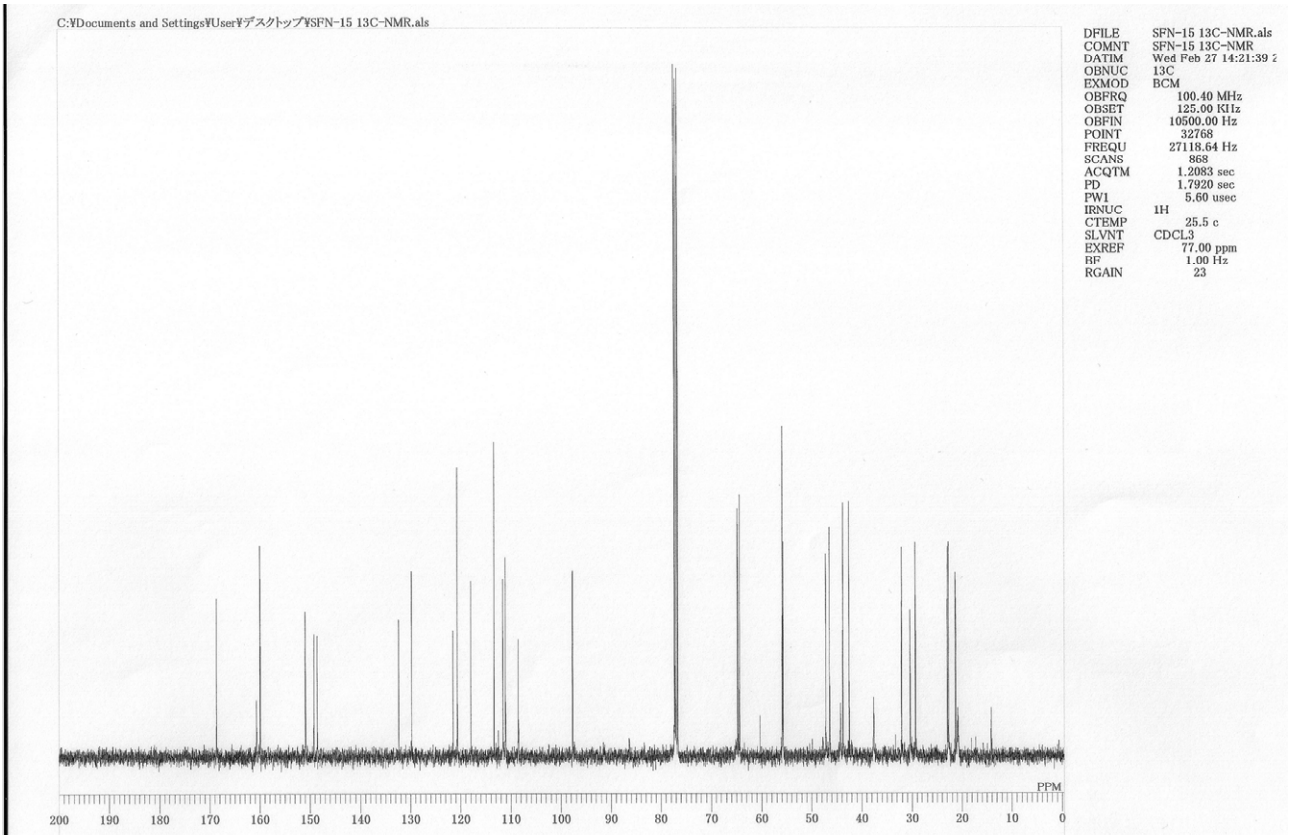

C:¥Documents and Settings¥User¥デスクトップ¥SFN-14 1H-NMR.als
3,4DMB
N
O
TBSO
OMe
Me
H
O
O
Me
O
12
DFILE SFN-14 1H-NMR.als
COMNT SFN-14
DATIM Sat Feb 09 17:08:53 2(
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.25 Hz
RGAIN 13
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-13 13C-NMR.als
DFILE SFN-13 13C-NMR.als
COMNT SFN-13 13C-NMR
DATIM Sat Feb 09 19:06:30 2(
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 1000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.25 Hz
RGAIN 25
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


¥¥10.20.93.90¥医薬合成化学¥SFN-14 1H pure.als
O
3,4DMB
N
MeO
Me
H
O
OH
O
O
Me
13
DFILE SFN-14 1H pure.als
COMNT auto
DATIM Sat Jun 27 14:01:13 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 6.00 usec
IRNUC 1H
CTEMP 26.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 18
PPM
8
7
6
5
4
3
2
1
0

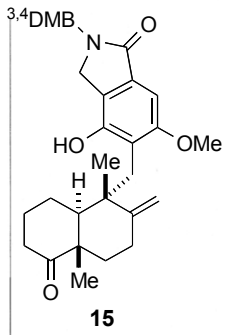

C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-14 13C-NMR.als
DFILE SFN-14 13C-NMR.als
COMNT SFN-14 13C-NMR
DATIM Tue Feb 12 18:45:13 2
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 1000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 25.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.25 Hz
RGAIN 24
PPM
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0


C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-15 1H-NMR.als
3,4DMB
N
O
HO
OMe
Me
H
O
O
Me
14
DFILE SFN-15 1H-NMR.als
COMNT SFN-15
DATIM Wed Feb 27 13:21:08 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 1.00 Hz
RGAIN 15
PPM
8
7
6
5
4
3
2
1
0


C:¥Documents and Settings¥User¥デスクトップ¥SFN-15 13C-NMR.als
DFILE SFN-15 13C-NMR.als
COMNT SFN-15 13C-NMR
DATIM Wed Feb 27 14:21:39 2
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 868
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 23
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

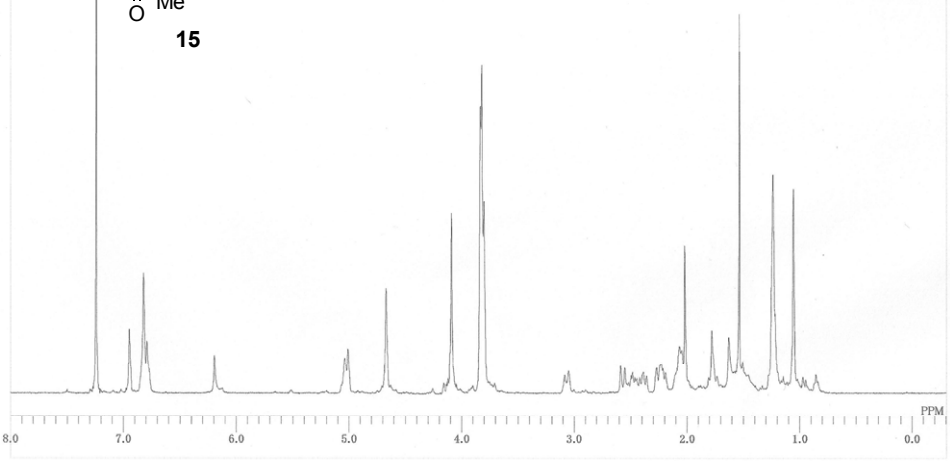
SFN-16

C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-16 1H-NMR.als



15

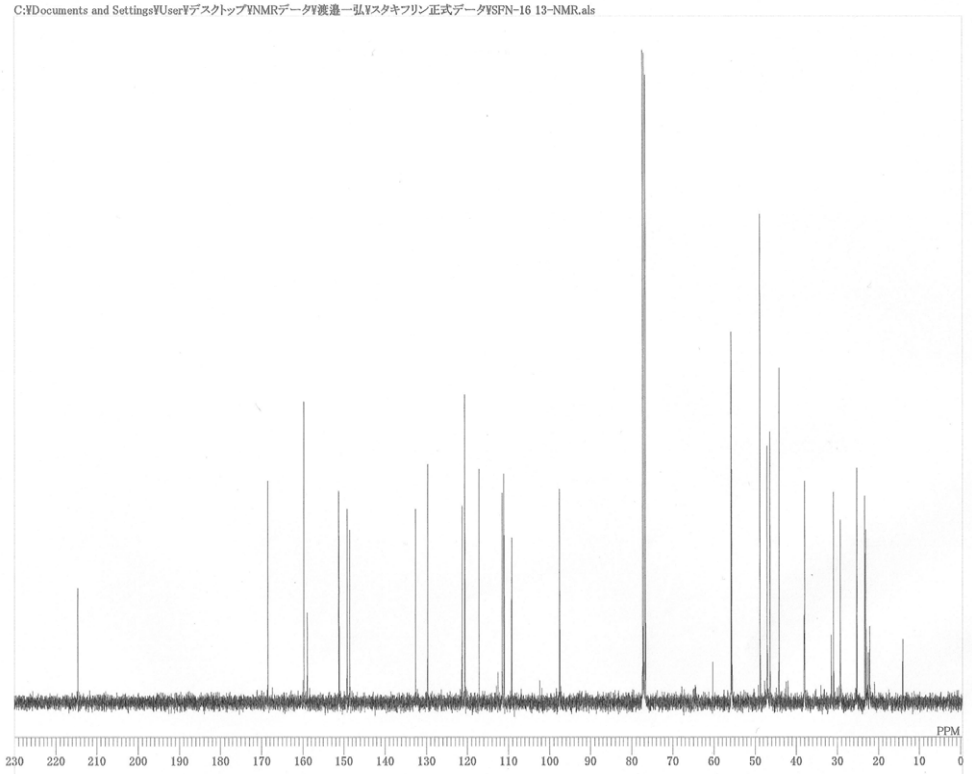
DFILE	SFN-16 1H-NMR.als
COMNT	SFN-16
DATIM	Thu Feb 28 12:44:43 2
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	16
ACQTM	2.0501 sec
PD	4.9500 sec
PW1	5.40 usec
IRNUC	1H
CTEMP	22.7 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.40 Hz
RGAIN	19

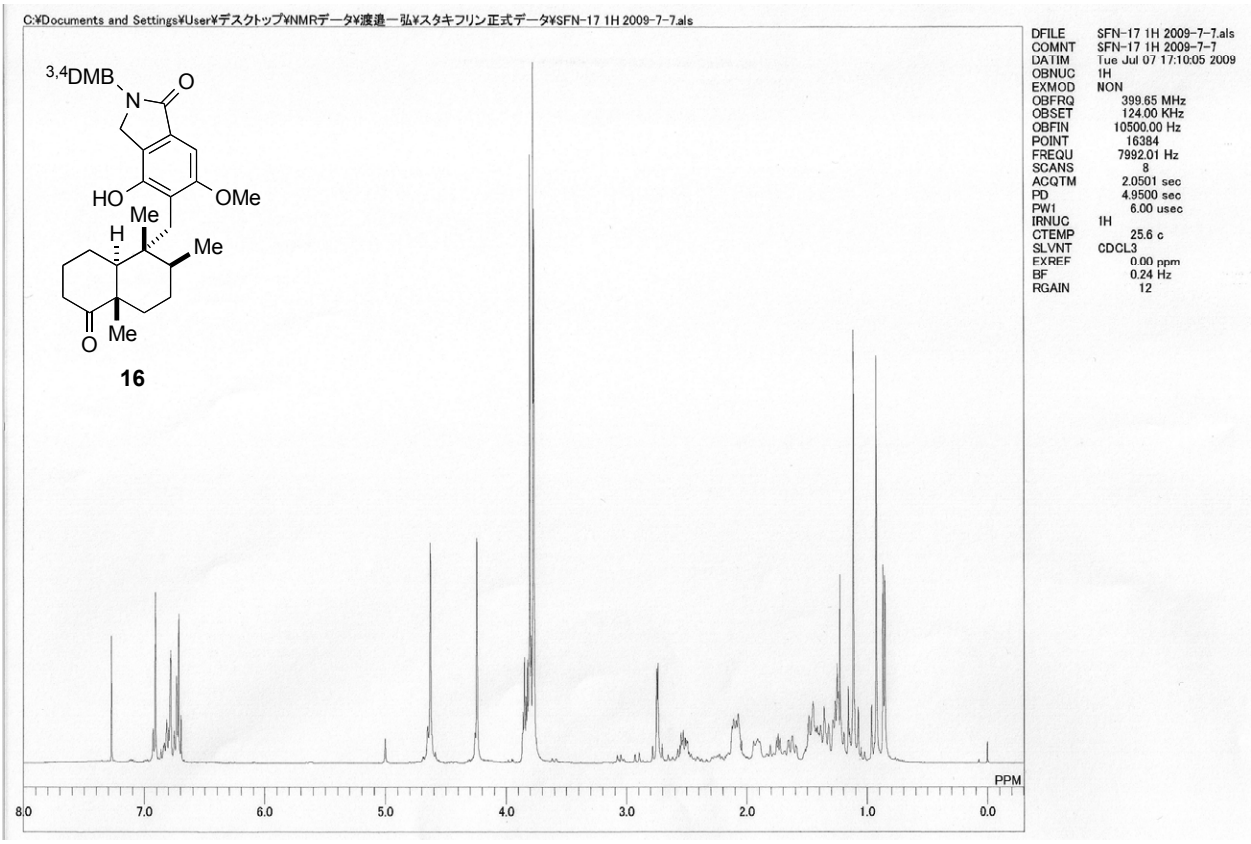


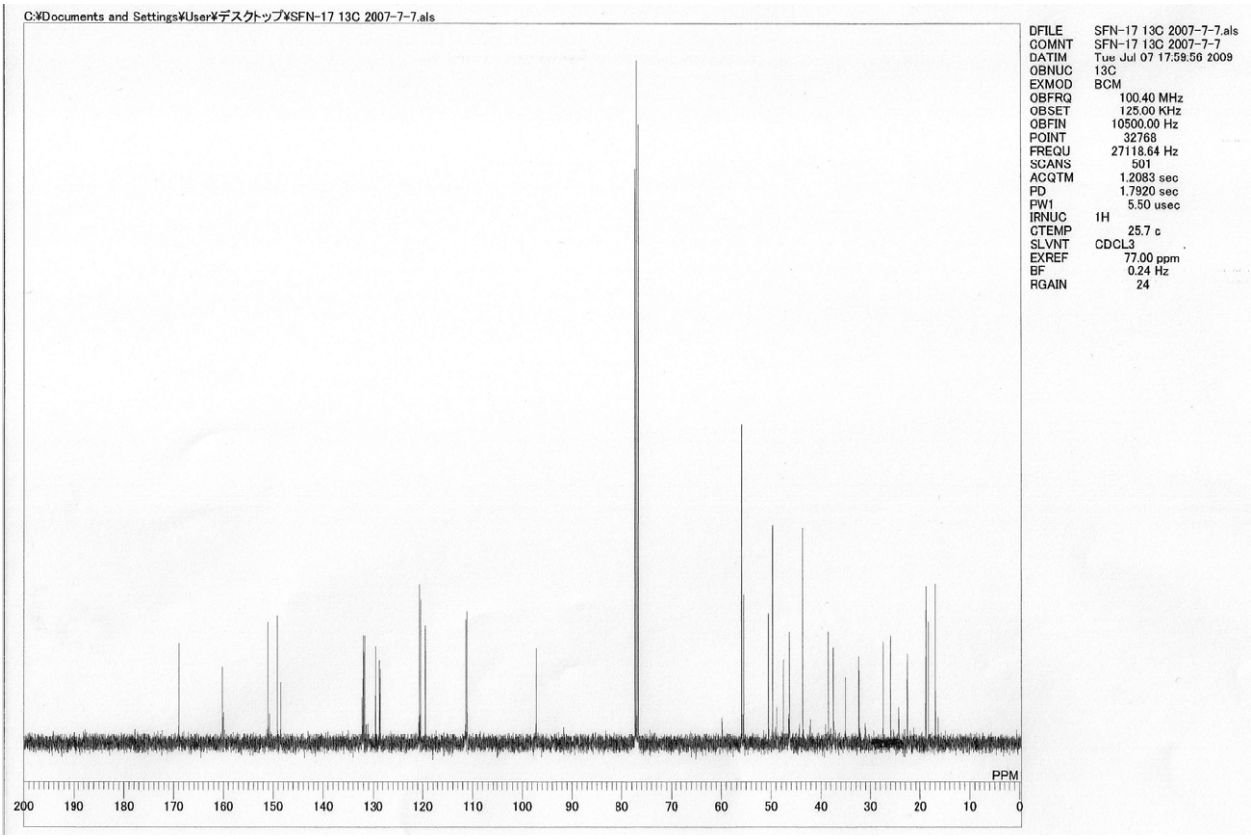
SFN-16 13C-NMR

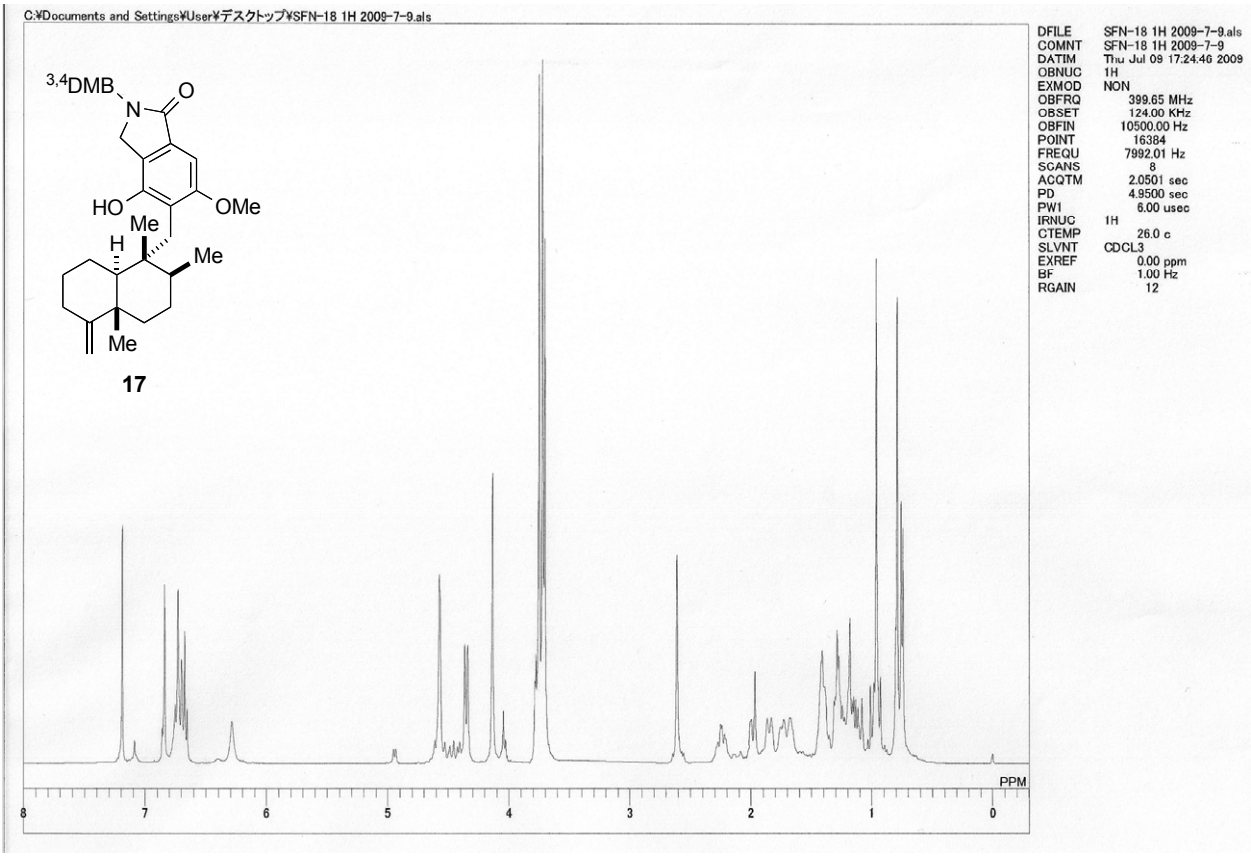
C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-16 13-NMR.als

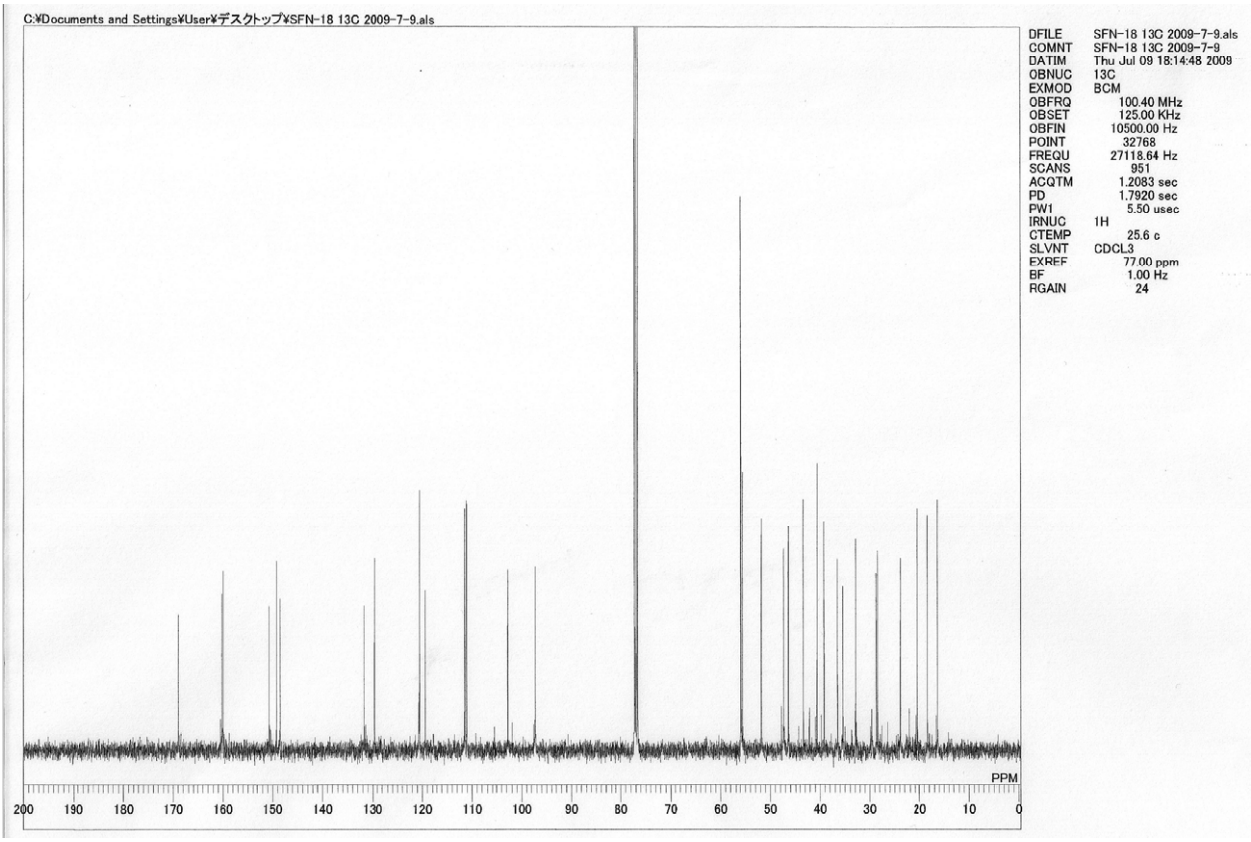
DFILE	SFN-16 13-NMR.als
COMNT	SFN-16 13C-NMR
DATIM	Thu Feb 28 13:53:34 2
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	1000
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	5.60 usec
IRNUC	1H
CTEMP	25.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.40 Hz
RGAIN	24

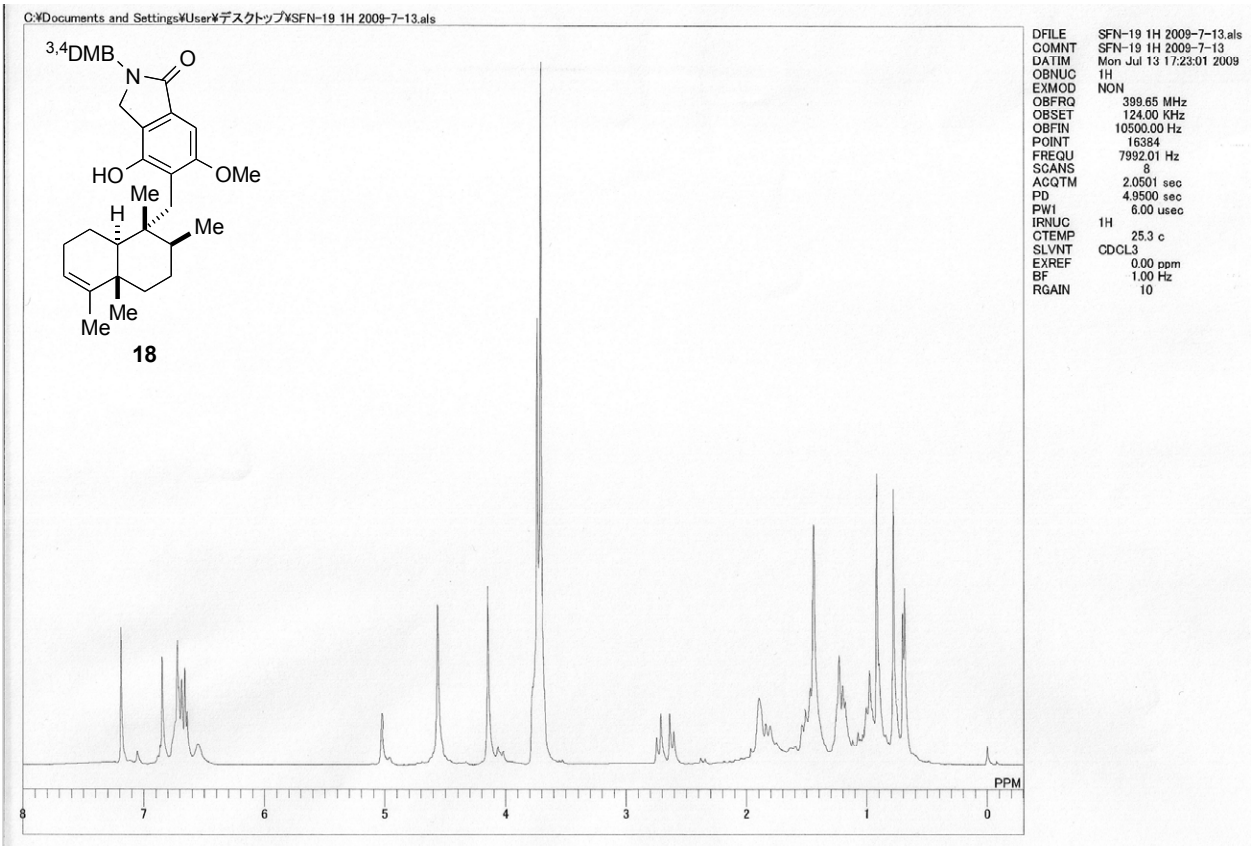


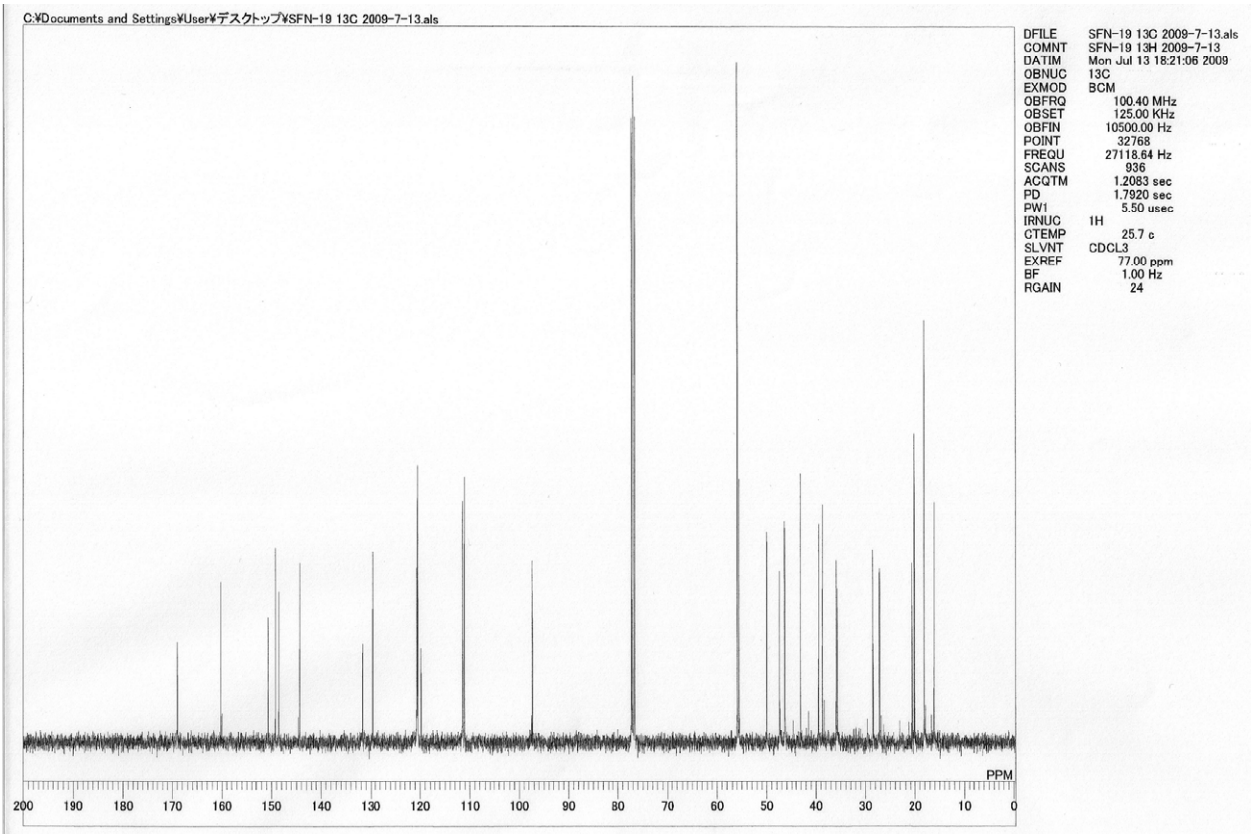

C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-17 1H 2009-7-7.als
3,4DMB
N
O
HO
OMe
Me
H
Me
O
Me
16
DFILE SFN-17 1H 2009-7-7.als
COMNT SFN-17 1H 2009-7-7
DATIM Tue Jul 07 17:10:05 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 6.00 usec
IRNUC 1H
CTEMP 25.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.24 Hz
RGAIN 12
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

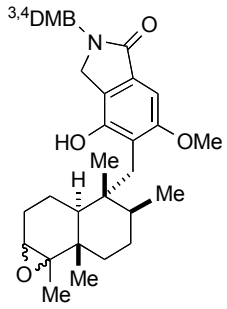

C:¥Documents and Settings¥User¥デスクトップ¥SFN-17 13C 2007-7-7.als
DFILE SFN-17 13C 2007-7-7.als
COMNT SFN-17 13C 2007-7-7
DATIM Tue Jul 07 17:59:56 2009
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 501
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.24 Hz
RGAIN 24
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


C:¥Documents and Settings¥User¥デスクトップ¥SFN-18 1H 2009-7-9.als
3,4DMB
N
O
HO
OMe
Me
H
Me
Me
17
DFILE SFN-18 1H 2009-7-9.als
COMNT SFN-18 1H 2009-7-9
DATIM Thu Jul 09 17:24:46 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 6.00 usec
IRNUC 1H
CTEMP 26.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 12
PPM
8 7 6 5 4 3 2 1 0

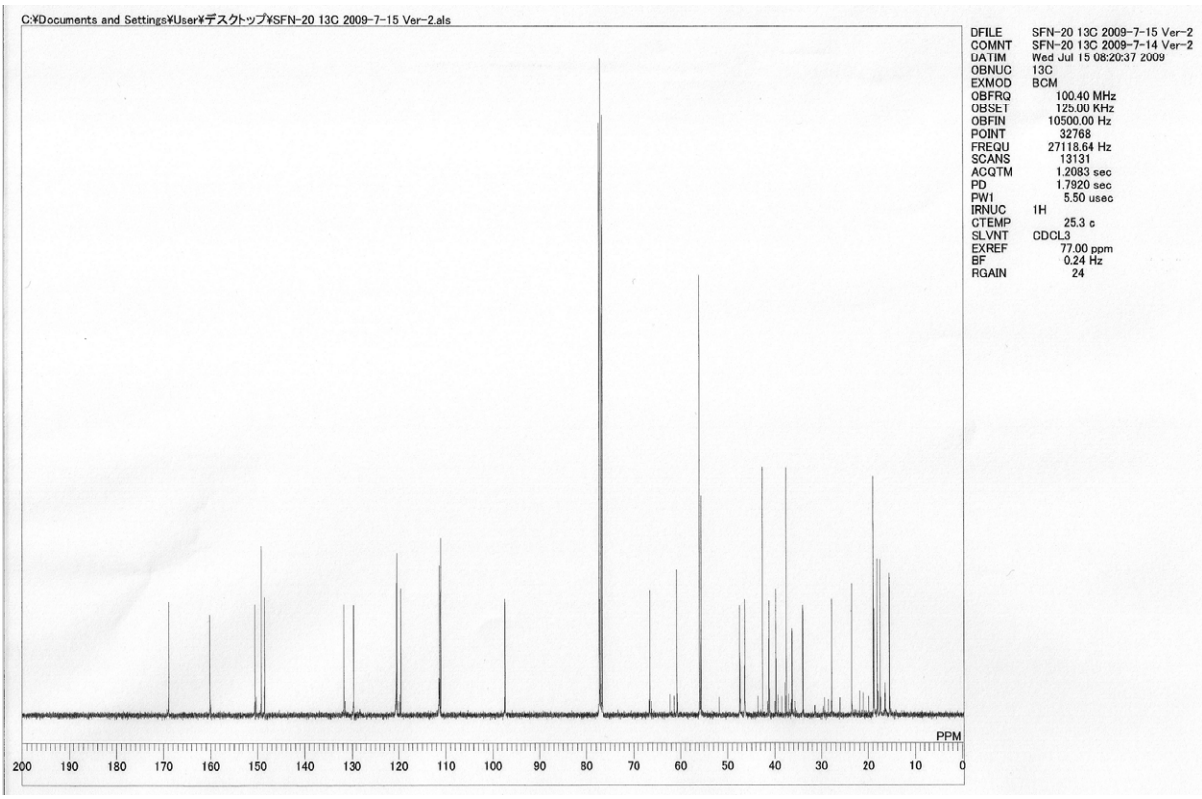

C:¥Documents and Settings¥User¥デスクトップ¥SFN-18 13C 2009-7-9.als
DFILE SFN-18 13C 2009-7-9.als
COMNT SFN-18 13C 2009-7-9
DATIM Thu Jul 09 18:14:48 2009
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 951
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 25.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 24
PPM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

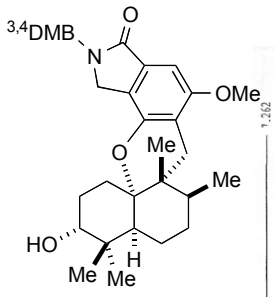

C:¥Documents and Settings¥User¥デスクトップ¥SFN-19 1H 2009-7-13.als
3,4DMB
N
O
HO
OMe
Me
H
Me
Me
Me
18
DFILE SFN-19 1H 2009-7-13.als
COMNT SFN-19 1H 2009-7-13
DATIM Mon Jul 13 17:23:01 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 6.00 usec
IRNUC 1H
CTEMP 25.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 10
PPM
8 7 6 5 4 3 2 1 0


C:¥Documents and Settings¥User¥デスクトップ¥SFN-19 13C 2009-7-13.als
DFILE SFN-19 13C 2009-7-13.als
COMNT SFN-19 13H 2009-7-13
DATIM Mon Jul 13 18:21:06 2009
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 936
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 24
PPM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

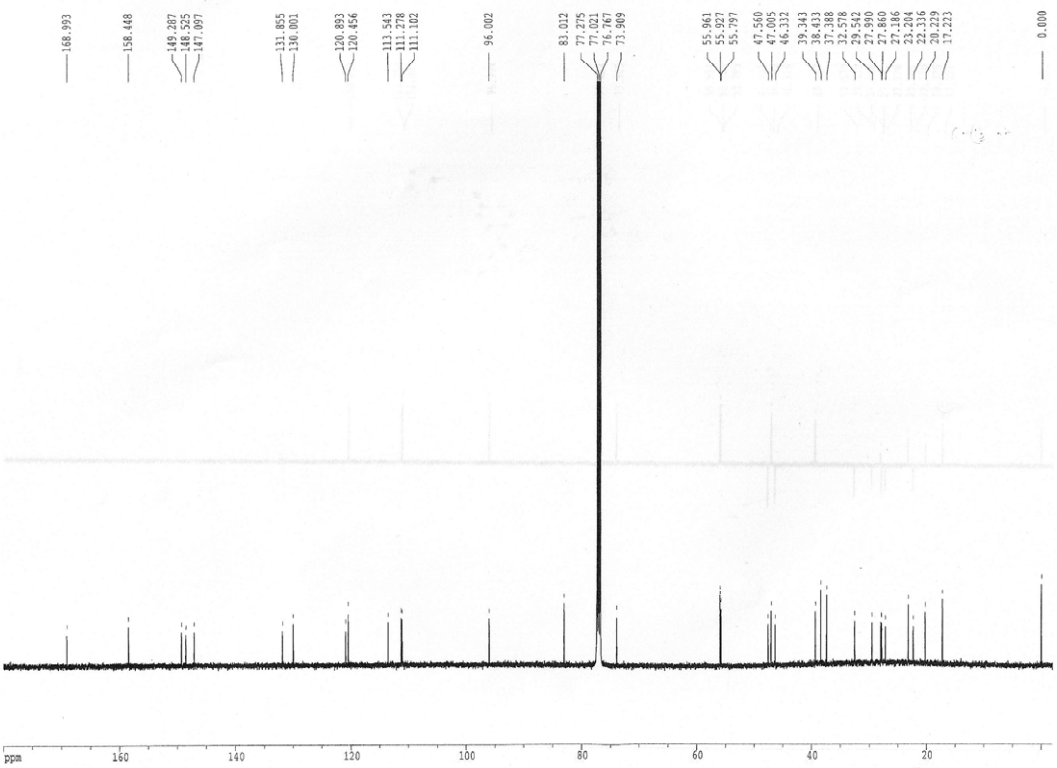


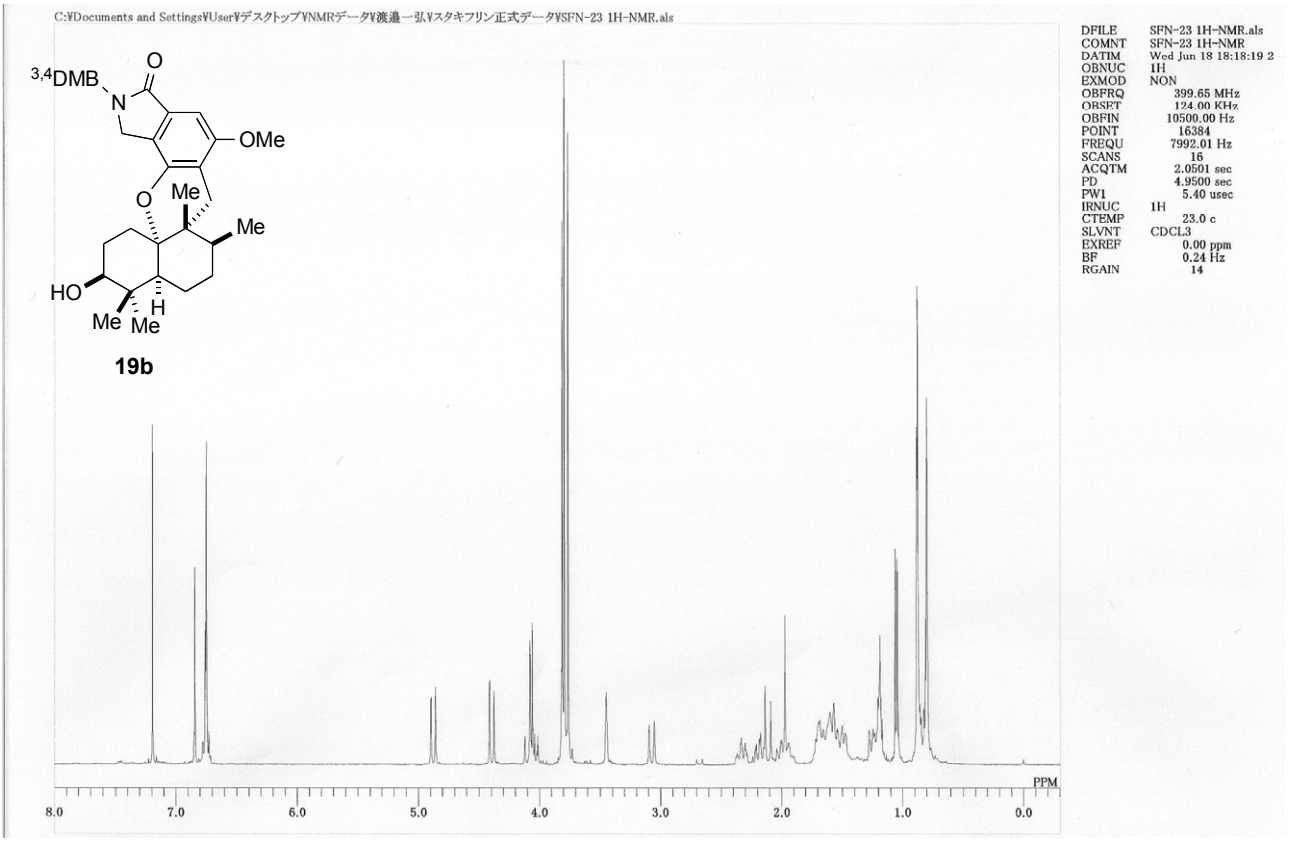
2 (α-/β-epoxide 7:1)

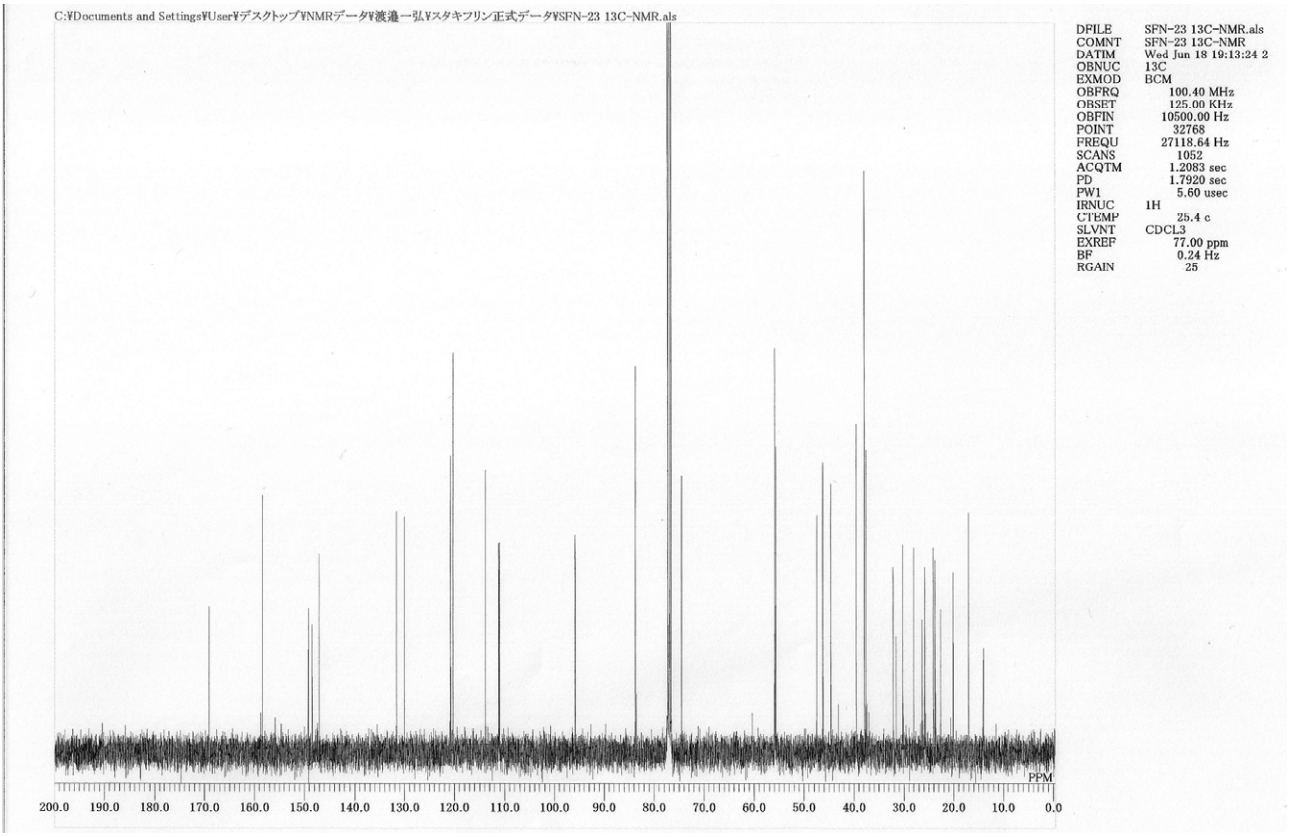


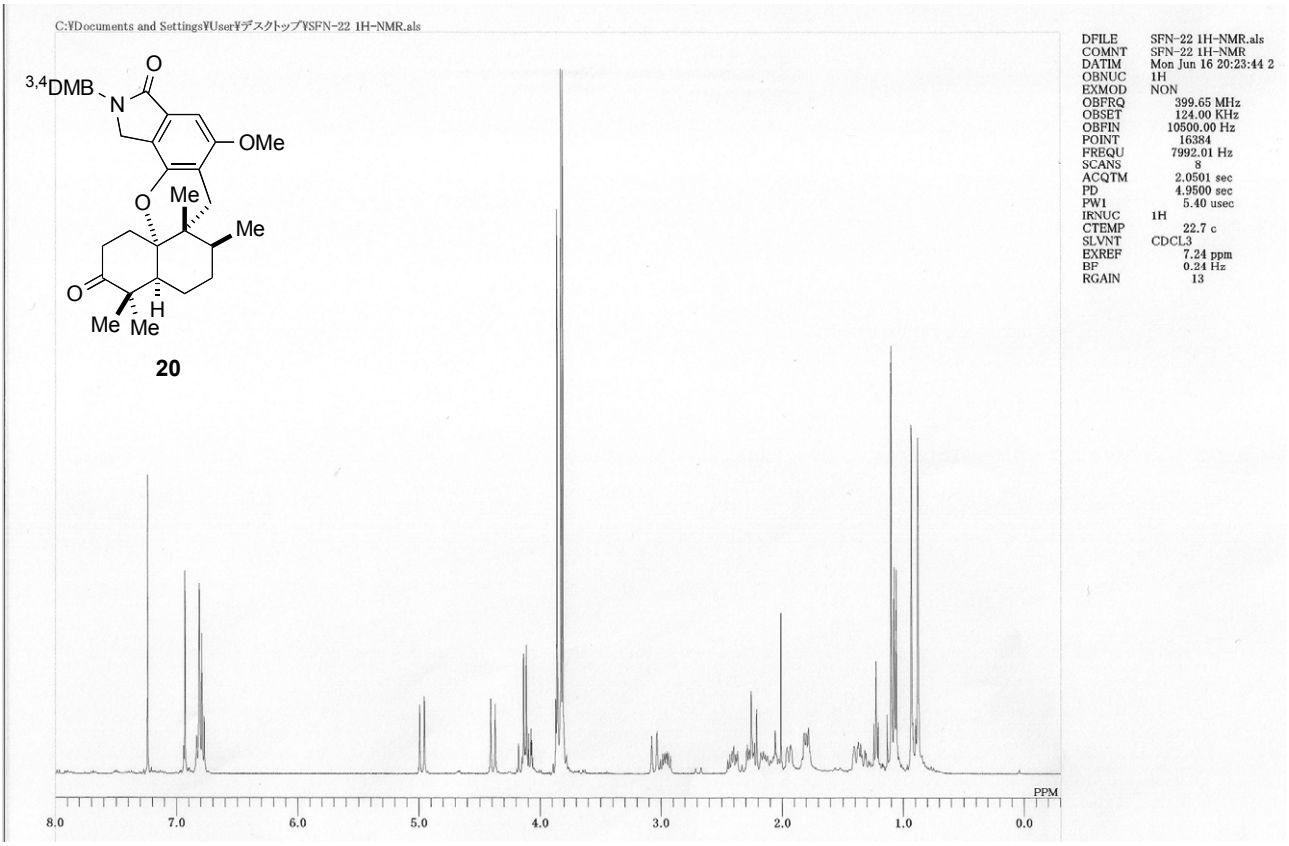


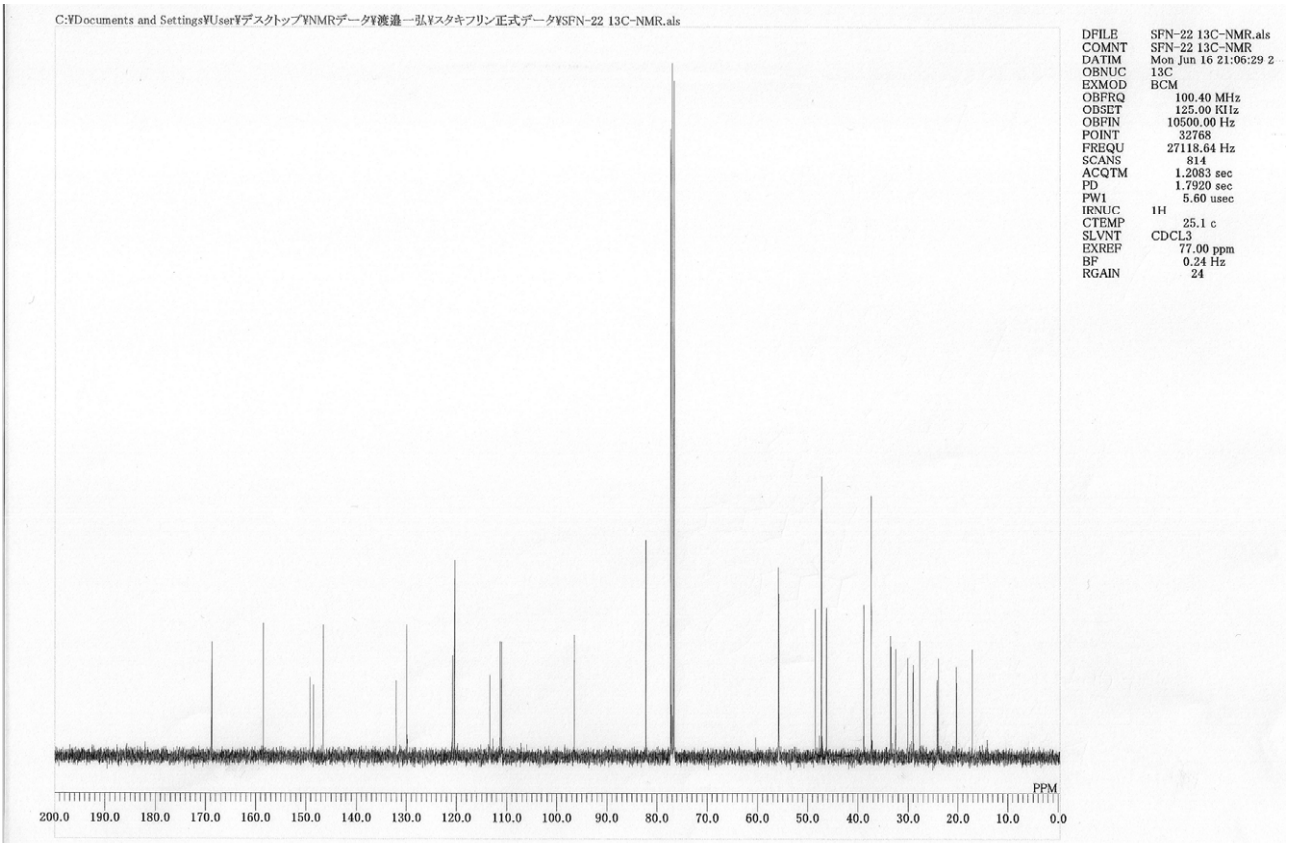
19a

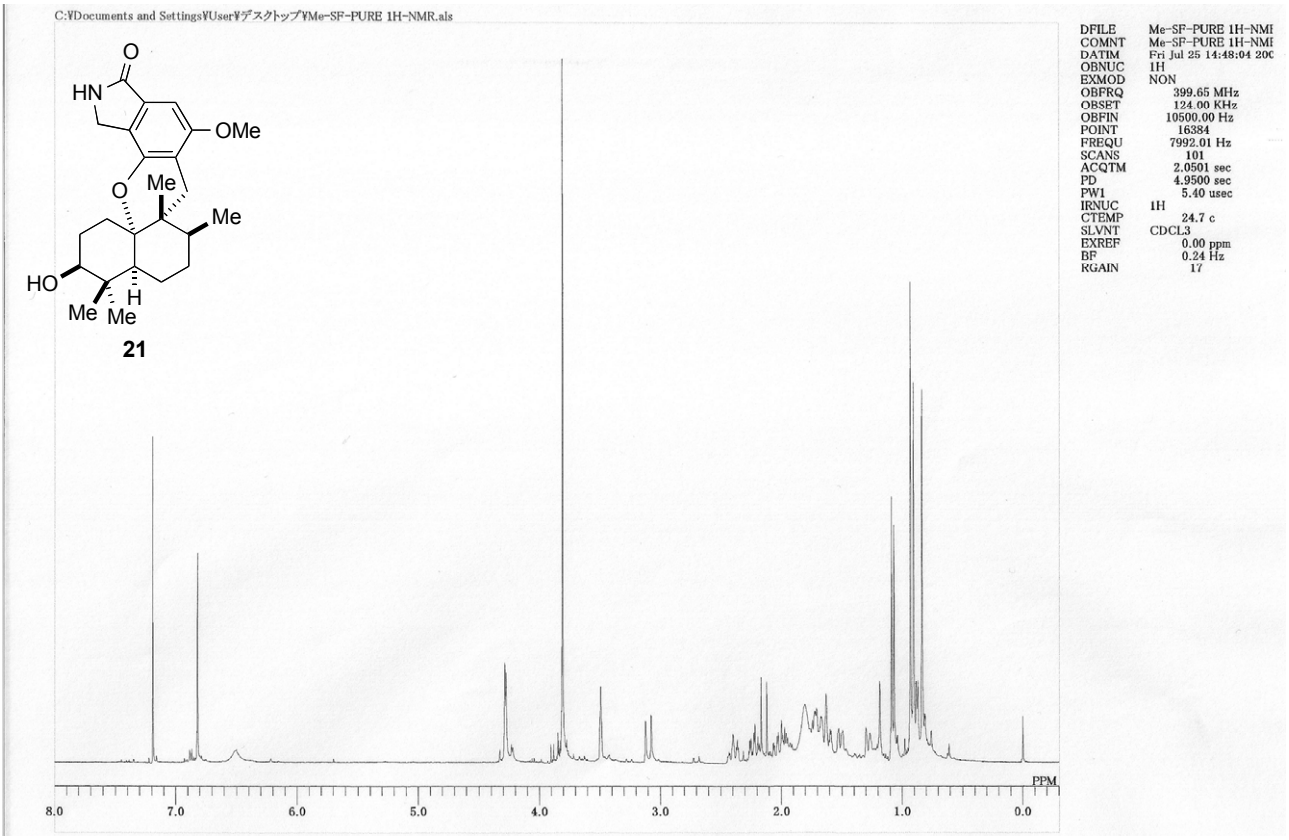


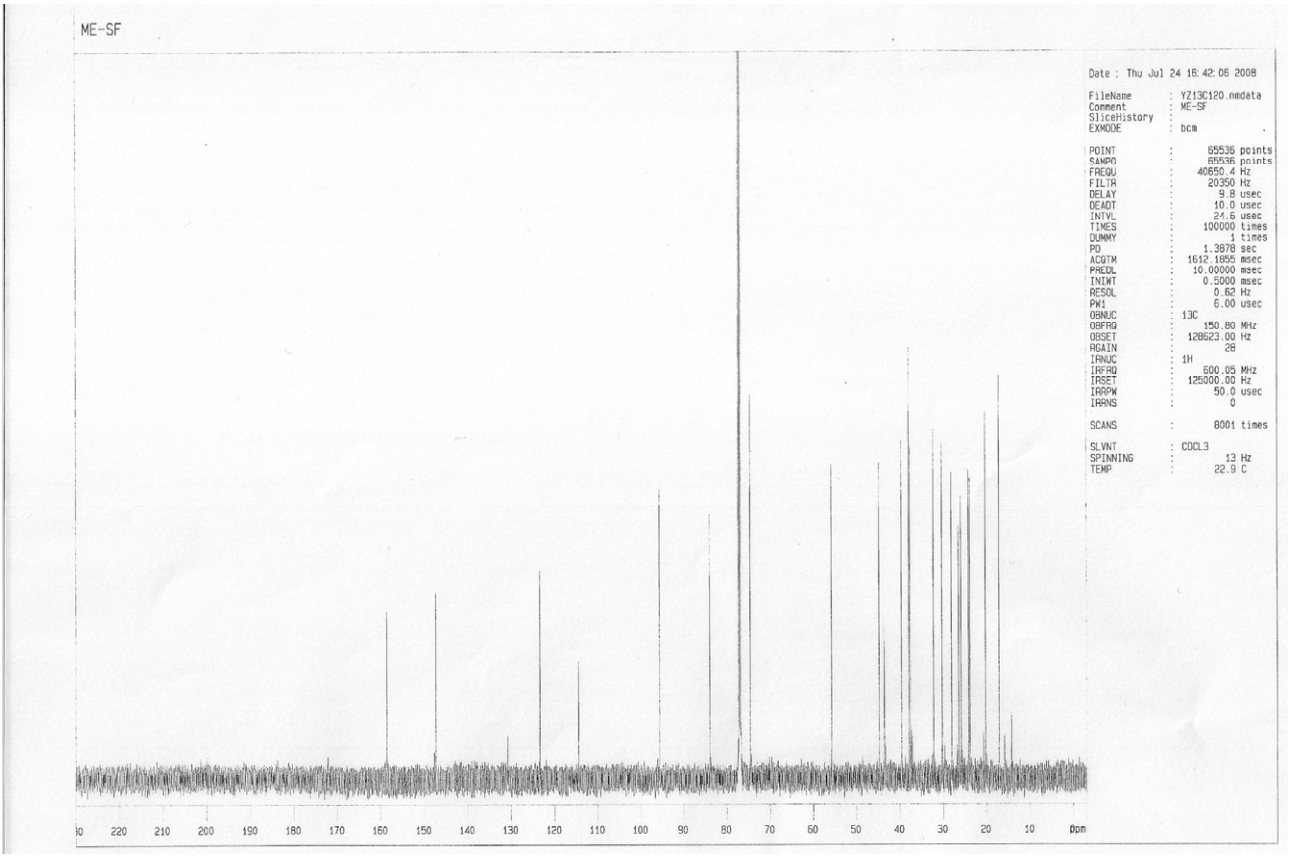

C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-23 1H-NMR.als
3,4DMB
N
O
OMe
O
Me
Me
HO
H
Me
Me
19b
DFILE SFN-23 1H-NMR.als
COMNT SFN-23 1H-NMR
DATIM Wed Jun 18 18:18:19 2
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 16
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.24 Hz
RGAIN 14
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

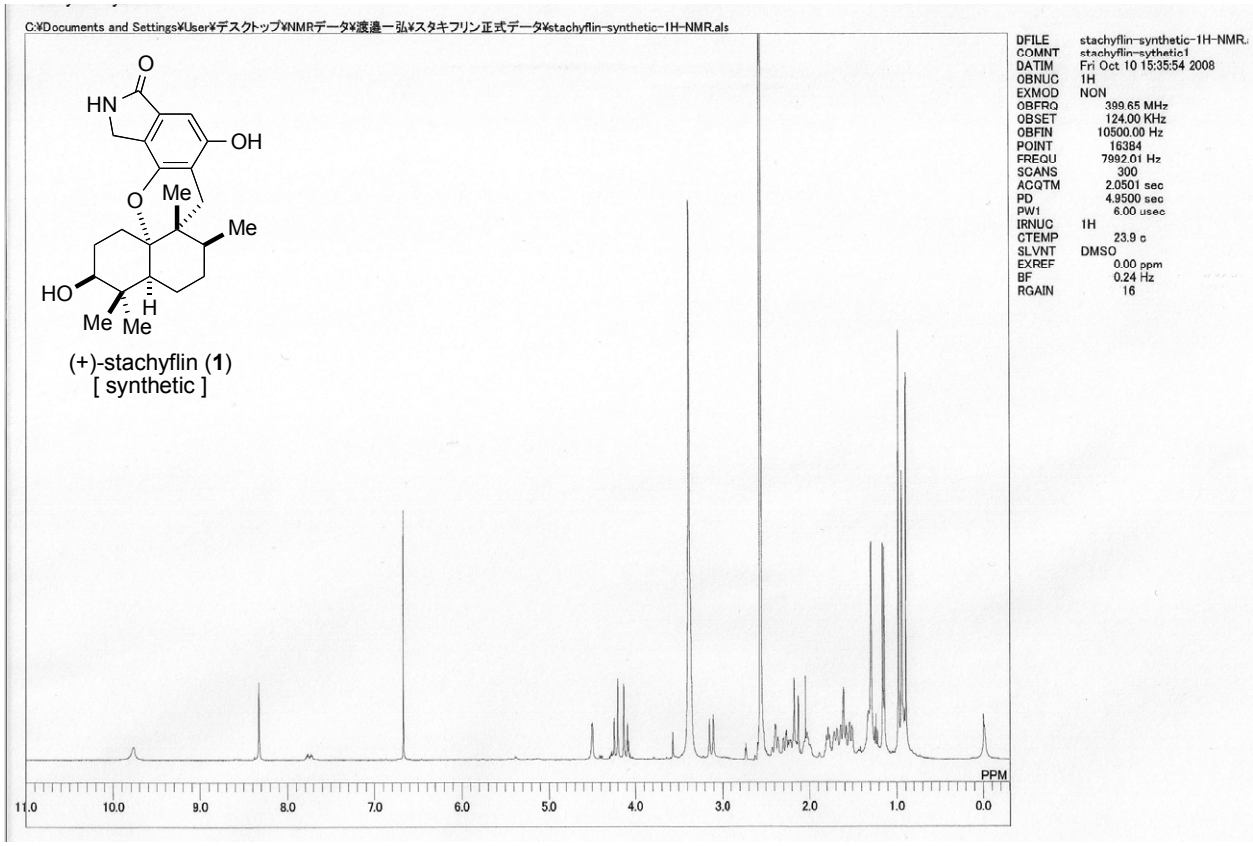

C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-23 13C-NMR.als
DFILE SFN-23 13C-NMR.als
COMNT SFN-23 13C-NMR
DATIM Wed Jun 18 19:13:24 2
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 1052
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 25.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.24 Hz
RGAIN 25
PPM
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0

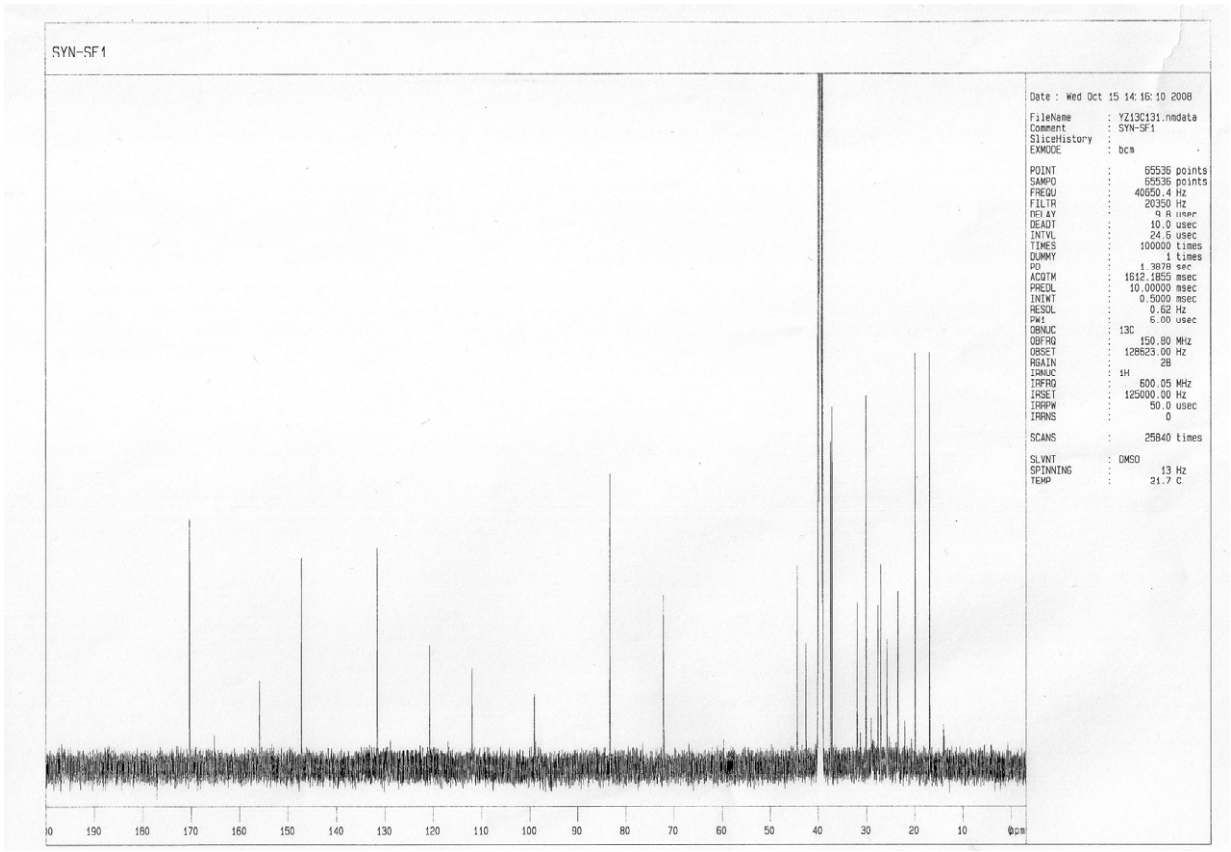

C:¥Documents and Settings¥User¥デスクトップ¥SFN-22 1H-NMR.als
3,4DMB
N
O
OMe
O
Me
Me
O
H
Me
Me
20
DFILE SFN-22 1H-NMR.als
COMNT SFN-22 1H-NMR
DATIM Mon Jun 16 20:23:44 2
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.24 Hz
RGAIN 13
PPM
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥SFN-22 13C-NMR.als
DFILE SFN-22 13C-NMR.als
COMNT SFN-22 13C-NMR
DATIM Mon Jun 16 21:06:29 2
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 814
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 25.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.24 Hz
RGAIN 24
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

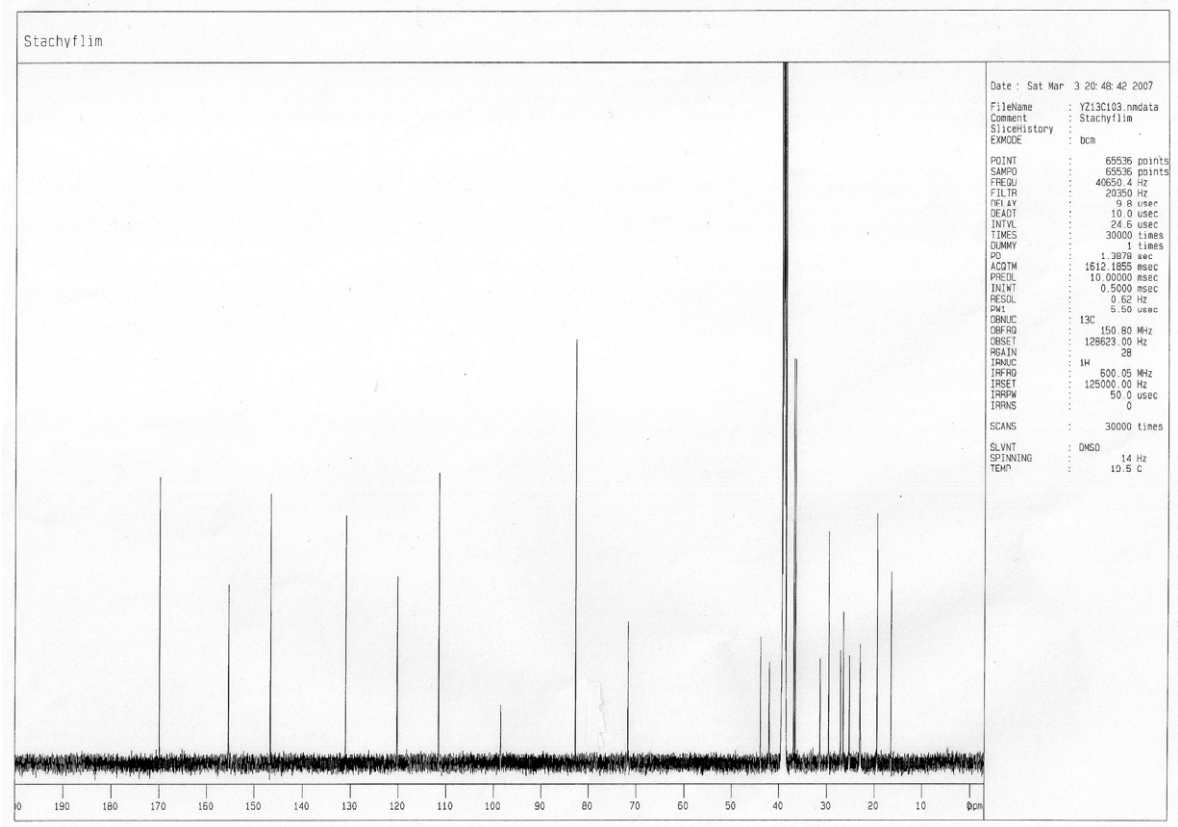

C:¥Documents and Settings¥User¥デスクトップ¥Me-SF-PURE 1H-NMR.als
O
HN
OMe
O
Me
Me
HO
Me
H
Me
21
DFILE Me-SF-PURE 1H-NMI
COMNT Me-SF-PURE 1H-NMI
DATIM Fri Jul 25 14:48:04 20C
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 101
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 24.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.24 Hz
RGAIN 17
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


ME-SF
Date : Thu Jul 24 16:42:06 2008
FileName : YZ13C120.nmdata
Comment : ME-SF
SliceHistory :
EXMODE : bcm
POINT : 65536 points
SAMPO : 65536 points
FREQU : 40650.4 Hz
FILTR : 20350 Hz
DELAY : 9.8 usec
DEADT : 10.0 usec
INTVL : 24.6 usec
TIMES : 100000 times
DUMMY : 1 times
PD : 1.3878 sec
ACQTM : 1612.1855 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.62 Hz
PW1 : 6.00 usec
OBNUC : 13C
OBFRQ : 150.80 MHz
OBSET : 128623.00 Hz
RGAIN : 28
IRNUC : 1H
IRFRQ : 600.05 MHz
IRSET : 125000.00 Hz
IRPPW : 50.0 usec
IRRNS : 0
SCANS : 8001 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 22.9 C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


C:¥Documents and Settings¥User¥デスクトップ¥NMRデータ¥渡邉一弘¥スタキフリン正式データ¥stachyflin-synthetic-1H-NMR.als
O
HN
OH
O
Me
Me
HO
H
Me
Me
(+)-stachyflin (1)
[synthetic]
DFILE stachyflin-synthetic-1H-NMR.
COMNT stachyflin-sythetic1
DATIM Fri Oct 10 15:35:54 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 300
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 6.00 usec
IRNUC 1H
CTEMP 23.9 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.24 Hz
RGAIN 16
PPM
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


SYN-SF1
Date : Wed Oct 15 14:16:10 2008
FileName : YZ13C131.nmdata
Comment : SYN-SF1
SliceHistory :
EXMODE : bcm
POINT : 65536 points
SAMPO : 65536 points
FREQU : 40650.4 Hz
FILTR : 20350 Hz
DELAY : 9.8 usec
DEADT : 10.0 usec
INTVL : 24.6 usec
TIMES : 100000 times
DUMMY : 1 times
PD : 1.3878 sec
ACQTM : 1612.1855 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.62 Hz
PW1 : 6.00 usec
OBNUC : 13C
OBFRQ : 150.80 MHz
OBSET : 128623.00 Hz
RGAIN : 28
IRNUC : 1H
IRFRQ : 600.05 MHz
IRSET : 125000.00 Hz
IRPPW : 50.0 usec
IRMNS : 0
SCANS : 25840 times
SLVNT : DMSO
SPINNING : 13 Hz
TEMP : 21.7 C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0ppm


Stachyflim
O
HN
OH
O
Me
Me
HO
H
Me
Me
(+)-stachyflin (1)
[natural]
Date : Fri Mar 2 19:45:29 2007
FileName : YZ1H184.nmdata
Comment : Stachyflim
SliceHistory :
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 12004.8 Hz
FILTR : 6000 Hz
DELAY : 33.3 usec
DEADT : 47.0 usec
INTVL : 83.3 usec
TIMES : 64 times
DUMMY : 1 times
PD : 4.2704 sec
ACQTM : 2729.5745 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.37 Hz
PW1 : 6.00 usec
OBNUC : 1H
OBFRQ : 600.05 MHz
OBSET : 125000.00 Hz
RGAIN : 22
SCANS : 64 times
SLVNT : DMSO
SPINNING : 13 Hz
TEMP : 19.0 C
1.06
1.39
1.19
1.16
1.06
1.06
28.52
1.11
1.05
3.39
1.16
1.10
1.00
1.24
3.43
3.38
3.33
10
9
8
7
6
5
4
3
2
1
0 ppm


Stachyflim
Date : Sat Mar 3 20:48:42 2007
FileName : YZ13C103.nmdata
Comment : Stachyflim
SliceHistory :
EXMODE : dcm
POINT : 65536 points
SAMPO : 65536 points
FREQU : 40650.4 Hz
FILTR : 20350 Hz
DELAY : 9.8 usec
DEADT : 10.0 usec
INTVL : 24.6 usec
TIMES : 30000 times
DUMMY : 1 times
PD : 1.3078 sec
ACQTM : 1612.1855 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.62 Hz
PW1 : 5.50 usec
OBNUC : 13C
OBFRQ : 150.80 MHz
OBSET : 128623.00 Hz
RGAIN : 28
IRNUC : 1H
IRFRQ : 600.05 MHz
IRSET : 125000.00 Hz
IRPPW : 50.0 usec
IRPNS : 0
SCANS : 30000 times
SLVNT : DMSO
SPINNING : 14 Hz
TEMP : 19.5 C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0ppm