Supporting Information

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The First Total Synthesis of Discorhabdin A

By Hirofumi Tohma, Yu Harayama, Miki Hashizume, Minako Iwata, Yorito Kiyono,
Masahiro Egi, and Yasuyuki Kita*

Complete experimental procedures and characterization data for all
previously unreported compounds described herein, including chiral
HPLC data for **26**

Experimental Section

General. Melting points were determined on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. Infrared (IR) absorption spectra were recorded as KBr pellets on a SHIMADZU FTIR-8400 spectrophotometer. NMR spectra were measured on a JEOL JMN-EX 270 or JEOL JNM-AL 300 or JEOL JNM-GSX 500. NMR spectra were obtained in CDCl₃ except where noted with TMS as an internal standard. Mass spectra (MS) were measured on a JEOL JMS-AMII50 or JEOL JMS-D300 instrument. E. Merck silica gel 60 for column chromatography and E. Merck precoated TLC plates, silica gel F₂₅₄ for preparative thin layer chromatography were used. Organic layers were dried with anhydrous MgSO₄ or Na₂SO₄. PIFA and iodosobenzene are commercially available. All reagents were of reagent grade, unless otherwise stated. In general, reactions were carried out in anhydrous solvents, unless otherwise mentioned.

2-(6-Hydroxy-1-oxo-2,3-dihydro-1*H*-1λ-benzo[*b*]thiophen-2-ylamino)-[1,4]-naphthoquinone (**5b**).

To a stirred solution of 2-[6-*tert*-butyldimethylsilanyloxy]-2,3-dihydrobenzo[*b*]-thiophen-2-ylamino] [1,4]naphthoquinone **5a** (4.7 mg, 0.0145 mmol) in anhydrous CH₂Cl₂ (1.0 mL) was added *m*-chloroperbenzoic acid (*m*CPBA) (3.7 mg, 0.0145 mmol) at 0°C under a nitrogen atmosphere. The mixture was stirred for 45 min at 0°C and then quenched with aqueous saturated Na₂S₂O₃ and extracted with AcOEt. The combined organics were dried and concentrated *in vacuo*. The residue was purified by flash chromatography (CH₂Cl₂/MeOH=20/1) to give **5b** (2.2 mg, 45%) as a yellow solid.

5a: a brown solid. mp 225-227 °C. IR (KBr): ν 3000-3500, 2922, 2851, 1676, 1603, 1572, 1502 cm⁻¹. ¹H NMR (300 MHz): δ 3.02 (br s, 1H), 3.31 (dd, 1H, *J* = 16.0, 2.0 Hz), 3.65 (dd, 1H, *J* = 15.5, 1.0 Hz), 5.37 (t, 1H, *J* = 8.5 Hz), 5.83 (s, 1H), 6.30 (d, 1H, *J* = 9.0 Hz), 6.57 (d, 1H, *J* = 7.5 Hz), 6.71 (br s, 1H), 7.12 (d, 1H, *J* = 8.5 Hz), 7.61 (t, 1H, *J* = 8.5, 6.5 Hz), 7.72 (t, 1H, *J* = 7.5, 6.5 Hz), 8.01 (d, 1H, *J* = 8.0 Hz), 8.09 (d, 1H, *J* = 8.0 Hz). ¹³C NMR (75 MHz): δ 41.8, 62.5, 104.1, 110.0, 112.3, 125.9, 126.3, 126.4, 127.9, 130.4, 132.4, 133.1, 134.9, 140.3, 145.8, 156.1, 181.3, 183.2. HRMS calcd for

C₂₀H₁₇NO₃ (M⁺) 323.0616, found 323.0612.

5b: IR (KBr): ν 3500-2700, 1678, 1607, 1574, 1493 cm⁻¹. ¹H NMR (300 MHz, CD₃OD): δ 3.67 (dd, 1H, J = 16.2, 6.9 Hz), 3.86 (dd, 1H, J = 15.9, 9.0 Hz), 5.34 (t, 1H, J = 7.2 Hz), 6.25 (s, 1H), 7.08 (dd, 1H, J = 8.4, 2.4 Hz), 7.31 (d, 1H, J = 2.4 Hz), 7.43 (d, 1H, J = 8.4 Hz), 7.76 (td, 1H, J = 7.5, 1.5 Hz), 7.83 (td, 1H, J = 7.5, 1.5 Hz), 8.07 (dd, 1H, J = 7.5, 1.2 Hz), 8.12 (dd, 1H, J = 7.5, 1.2 Hz). HR-FABMS calcd for C₁₈H₁₃NO₄Na (M+Na⁺); 362.0463, found 362.0449. This compound gradually decomposed during ¹³C NMR measurement due to its unstability.

2-(1,4-Dioxo-1,4-dihydronaphthalen-2-ylamino)-3-(4-hydroxyphenyl)propionic acid methyl ester (7).

To a stirred solution of **6** (1.05 g, 5.40 mmol) in MeOH (8.0 mL) was added 1,4-naphthoquinone (854 mg, 5.40 mmol) at room temperature, and the mixture was stirred overnight (for 12 h) under the same conditions. The resulting mixture was concentrated *in vacuo*, then the residue was purified by column chromatography (*n*-hexane/AcOEt=3:1) to give **7** (1.08 g, 57%) as a brown solid.

7: mp 70-72 °C (from EtOH). IR (KBr): ν 3354, 1746, 1678, 1607, 1568, 1514 cm⁻¹. ¹H NMR (300 MHz): δ 3.07 (dd, 1H, J = 14.0, 6.5 Hz), 3.17 (dd, 1H, J = 14.0, 5.5 Hz), 3.74 (s, 3H), 4.21-4.30 (m, 1H), 5.66 (s, 1H), 6.14 (s, 1H), 6.33 (d, 1H, J = 8.0 Hz), 6.77 (d, 2H, J = 8.5 Hz), 6.98 (d, 2H, J = 8.5 Hz), 7.61 (t, 1H, J = 7.5 Hz), 7.71 (t, 1H, J = 7.5 Hz), 8.03 (d, 1H, J = 7.6 Hz), 8.07 (d, 1H, J = 7.6 Hz). ¹³C NMR (75 MHz): δ 36.7, 52.7, 56.2, 101.9, 115.9, 126.2, 126.5, 126.6, 130.3, 130.4, 132.3, 133.2, 134.8, 146.8, 155.4, 170.8, 181.1, 183.5. HRMS calcd for C₂₀H₁₇NO₃ (M⁺) 351.1106, found 351.1116.

1,2,3,4,5,10-Hexahydrobenzo[6,7-g]quinoline-5,10-dione-2-carboxyl-4-spiro4'-cyclohexa-2',5'-dien-1'-one (8).

To a stirred solution of **6** (53.8 mg, 0.153 mmol) in CF₃CH₂OH (5.0 mL) was added MK10 (33.6 mg) and PIFA (98.8 mg, 0.230 mmol) sequentially at room temperature under a nitrogen atmosphere. The mixture was stirred for 30 min and then concentrated

in vacuo. The residue was purified by column chromatography (*n*-hexane/AcOEt=1:1) to give 1,2,3,4,5,10-hexahydrobenzo[6,7-*g*]quinoline-5,10-dione-2-methoxycarbonyl-4-spiro4'-cyclohexa-2',5'-dien-1'-one (22.5 mg, 42%) as a red solid.

mp 93-96 °C (from AcOEt). IR (KBr): ν 1745, 1661, 1601, 1570, 1504 cm^{-1} . ^1H NMR (300 MHz): δ 2.03-2.21 (m, 2H), 3.85 (s, 3H), 4.28 (dd, 1H, $J = 10.0, 4.0$ Hz), 6.39 (d, 1H, $J = 10.0$ Hz), 6.43 (d, 1H, $J = 10.0$ Hz), 6.73 (s, 1H), 6.85 (dd, 1H, $J = 10.0, 3.0$ Hz), 6.92 (dd, 1H, $J = 10.0, 3.0$ Hz), 7.61 (t, 1H, $J = 7.5$ Hz), 7.71 (t, 1H, $J = 7.5$ Hz), 7.99 (d, 1H, $J = 7.5$ Hz), 8.04 (d, 1H, $J = 7.0$ Hz). ^{13}C NMR (75 MHz): δ 36.5, 40.0, 50.2, 53.2, 110.2, 126.1, 126.5, 128.1, 129.0, 129.8, 132.3, 133.2, 135.2, 144.0, 149.8, 153.6, 170.2, 179.7, 180.1, 185.2. HRMS calcd for $\text{C}_{20}\text{H}_{13}\text{NO}_3$ (M^+) 349.0950, found 349.0965.

To a stirred solution of 1,2,3,4,5,10-hexahydrobenzo[6,7-*g*]quinoline-5,10-dione-2-methoxycarbonyl-4-spiro4'-cyclohexa-2',5'-dien-1'-one (18.1 mg, 0.0518 mmol) in 1,4-dioxane (1.5 mL) was added 6N HCl (1.5 mL) at room temperature. The mixture was stirred at 60°C for 2.5 h, then cooled to room temperature, and extracted with AcOEt. The combined organic layer was washed with brine, dried, and evaporated *in vacuo*. The residue was purified by column chromatography (AcOEt/AcOH=100:1) to give **8** (13.2 mg, 76%) as an orange solid.

8: mp 205-207 °C. IR (KBr): ν 2873, 1736, 1657, 1599, 1568, 1502 cm^{-1} . ^1H NMR (500 MHz, CD_3OD): δ 2.16 (d, 2H, $J = 6.5$ Hz), 4.38 (t, 1H, $J = 6.0$ Hz), 6.32 (d, 2H, $J = 10.0$ Hz), 7.04 (dd, 1H, $J = 10.0, 2.5$ Hz), 7.17 (dd, 1H, $J = 10.0, 2.5$ Hz), 7.66 (td, 1H, $J = 7.5, 1.0$ Hz), 7.73 (td, 1H, $J = 7.5, 1.0$ Hz), 7.90 (d, 1H, $J = 7.0$ Hz), 8.04 (d, 1H, $J = 6.5$ Hz). ^{13}C NMR (75 MHz, CD_3OD): δ 37.3, 42.0, 51.5, 109.7, 127.1, 128.4, 128.6, 131.6, 133.4, 134.9, 136.1, 146.7, 154.9, 157.0, 181.0, 181.4, 188.1. HRMS calcd for $\text{C}_{19}\text{H}_{14}\text{NO}_3$ (M^+) 336.0872, found 332.0875.

1,2,3,4,5,10-Hexahydrobenzo[6,7-*g*]quinoline-5,10-dione-2-methoxy-4-spiro4'-cyclohexa-2',5'-dien-1'-one (10).

A solution of **8** (7.7 mg, 0.023 mmol) in MeOH (5.0 mL) containing NaOMe (0.062 mg, 1.15×10^{-3} mmol) was electrolyzed at room temperature using a 6.4 cm² of graphite anode-graphite cathode system in a non-divided cell under a nitrogen atmosphere. The electrolysis current was maintained at 1.0 mA during the electrolysis. After the theoretical amount of electricity had passed (for 74 min), the electrolyzed solution was evaporated to dryness *in vacuo*. The residue was purified by column chromatography (*n*-hexane/AcOEt=1:1) to give **10** (4.4 mg, 60%) as a yellow solid

10: mp 192-195 °C (from AcOEt). IR (KBr): ν 3360, 1660, 1605, 1575, 1505 cm⁻¹. ¹H NMR (300 MHz): δ 2.00 (d, 1H, J = 14.0 Hz), 2.09 (dd, 1H, J = 14.0, 3.5 Hz), 3.42 (s, 3H), 4.84-4.88 (m, 1H), 6.31 (dd, 1H, J = 10.0, 1.8 Hz), 6.43 (dd, 1H, J = 10.0, 1.8 Hz), 6.84 (dd, 1H, J = 10.0, 3.0 Hz), 6.90 (br s, 1H), 7.25 (dd, 1H, J = 10.0, 3.0 Hz), 7.63 (td, 1H, J = 7.6, 1.2 Hz), 7.72 (td, 1H, J = 7.6, 1.2 Hz), 8.02 (d, 1H, J = 7.5 Hz), 8.05 (d, 1H, J = 7.5 Hz). ¹³C NMR (67 MHz): δ 38.1, 39.3, 55.2, 79.3, 112.3, 126.0, 126.5, 127.6, 127.8, 129.8, 132.3, 132.9, 135.1, 142.5, 151.8, 154.1, 180.2, 185.6. HRMS calcd for C₁₉H₁₃NO₄ (M⁺) 321.1001, found 321.1018.

2-[1-(tert-Butyldimethylsilanyloxymethyl)-2-[4-(tert-butyldimethylsilanyloxy)phenyl]ethylamino][1,4]naphthoquinone (11).

A solution of **7** (203 mg, 0.578 mmol) in anhydrous THF (10 mL) was added to a stirred suspension of LiBH₄ (57.0 mg, 2.62 mmol) in anhydrous THF (5.0 mL) at 0°C under a nitrogen atmosphere. The mixture was stirred for 2 h at room temperature and then quenched with THF saturated with water at 0°C and extracted with AcOEt. The combined organics were washed with brine, dried and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=1/1) to give 2-[1-hydroxymethyl-2-(4-hydroxyphenyl)ethylamino][1,4]naphthoquinone (187 mg, quant) as a red crystal.

mp 167-169 °C. IR (KBr): ν 3345, 2500, 1680, 1600, 1570, 1515 cm⁻¹. ¹H NMR (270 MHz, CD₃OD): δ 2.78 (dd, 1H, J = 14.5, 8.0 Hz), 2.89 (dd, 1H, J = 14.0, 6.5 Hz), 3.62-3.70 (m, 3H), 5.66 (s, 1H), 5.67 (s, 1H), 6.68 (d, 2H, J = 8.5 Hz), 7.07 (d, 2H, J = 8.5

Hz), 7.65 (td, 1H, $J = 7.5, 1.5$ Hz), 7.75 (td, 1H, $J = 7.5, 1.5$ Hz), 7.97 (d, 1H, $J = 7.5$ Hz), 8.02 (d, 1H, $J = 7.5$ Hz). ^{13}C NMR (67 MHz, CD_3OD): δ 36.8, 57.5, 63.3, 100.4, 116.2, 126.6, 127.2, 129.6, 131.2, 131.8, 133.2, 134.6, 135.7, 150.1, 157.0, 182.2, 184.6. HR-FABMS calcd for $\text{C}_{19}\text{H}_{13}\text{NO}_4$ ($\text{M}+\text{H}^+$); 324.1236, found 324.1232.

To a stirred solution of 2-[1-hydroxymethyl-2-(4-hydroxyphenyl)ethylamino]-[1,4]naphthoquinone (3.37 g, 10.4 mmol) in anhydrous CH_2Cl_2 (150 mL) was added *tert*-butyldimethylsilyl chloride (TBSCl) (4.71 g, 31.3 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (7.8 mL, 52.0 mmol) sequentially at 0°C under a nitrogen atmosphere. The mixture was stirred for 1 h at room temperature and then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=30/1) to give **11** (5.75 g, quant) as an orange oil.

11: IR (KBr): ν 2953, 2856, 1678, 1607, 1574, 1504 cm^{-1} . ^1H NMR (500 MHz): δ 0.05 (s, 6H), 0.14 (s, 3H), 0.15 (s, 3H), 0.93 (s, 9H), 0.94 (s, 9H), 2.85-2.87 (m, 2H), 3.56 (m, 1H), 3.61 (d, 2H, $J = 3.5$ Hz), 5.75 (s, 1H), 6.25 (d, 1H, $J = 9.0$ Hz), 6.75 (d, 2H, $J = 8.5$ Hz), 7.05 (d, 2H, $J = 8.0$ Hz), 7.59 (t, 1H, $J = 7.5$ Hz), 7.70 (t, 1H, $J = 7.5$ Hz), 8.02 (d, 1H, $J = 7.5$ Hz), 8.08 (d, 1H, $J = 7.0$ Hz). ^{13}C NMR (125 MHz): δ -5.50, -5.42, -4.47, 18.2, 25.7, 25.9, 35.4, 54.9, 61.9, 100.9, 120.3, 126.2, 126.3, 129.9, 130.3, 130.6, 131.9, 133.7, 134.7, 147.1, 154.5, 181.8, 183.0. HRMS calcd for $\text{C}_{31}\text{H}_{43}\text{NO}_4\text{Si}_2$ (M^+) 551.2887, found 551.2888.

1,2,3,4,5,10-Hexahydrobenzo[6,7-*g*]quinoline-5,10-dione-2-hydroxymethyl-4-spiro-4'-cyclohexa-2',5'-dien-1'-one (12).

To a stirred solution of **11** (52.9 mg, 0.0959 mmol) in $\text{CF}_3\text{CH}_2\text{OH}$ (1.0 mL) was added PIFA (49.5 mg, 0.115 mmol) at room temperature under a nitrogen atmosphere. The mixture was stirred for 0.5 h and then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=2/1) to give 1,2,3,4,5,10-hexahydrobenzo[6,7-*g*]quinoline-5,10-dione-2-*tert*-butyl-dimethylsilyloxymethyl-4-spiro-4'-cyclohexa-2',5'-dien-1'-one (29.7 mg, 71%) as a red solid.

mp 63-67 °C. IR (KBr): ν 2952, 2852, 1661, 1599, 1568, 1497 cm^{-1} . ^1H NMR (500 MHz): δ 0.10 (s, 3H), 0.12 (s, 3H), 0.94 (s, 9H), 1.61 (dd, 1H, $J = 12.5, 2.0$ Hz), 1.76 (dd, 1H, $J = 13.0, 11.5$ Hz), 3.53 (dd, 1H, $J = 10.0, 9.0$ Hz), 3.64-3.69 (m, 1H), 3.85 (dd, 1H, $J = 10.0, 4.0$ Hz), 6.31 (d, 1H, $J = 9.5$ Hz), 6.40 (d, 1H, $J = 9.0$ Hz), 6.68 (brs, 1H), 6.89-6.94 (m, 2H), 7.57 (d, 1H, $J = 7.5$ Hz), 7.67 (d, 1H, $J = 7.5$ Hz), 7.98 (d, 1H, $J = 8.5$ Hz), 8.00 (d, 1H, $J = 8.0$ Hz). ^{13}C NMR (125 MHz): δ -5.49, -5.37, 18.2, 25.8, 36.6, 40.2, 49.6, 65.7, 109.8, 125.9, 126.5, 127.3, 128.7, 130.0, 132.0, 133.6, 135.1, 144.8, 150.4, 155.4, 179.5, 180.6, 185.5. HRMS calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_4\text{Si}$ (M^+) 435.1866, found 435.1872.

To a stirred solution of 1,2,3,4,5,10-hexahydrobenzo[6,7-*g*]quinoline-5,10-dione-2-*tert*-butyl-dimethylsilyloxymethyl-4-spiro-4'-cyclohexa-2',5'-dien-1'-one (2.0 g, 4.94 mmol) in THF (100 mL)- H_2O (1.0 mL) was added tetra *n*-buthylammonium fluoride (TBAF) (1M solution in THF) (5.0 mL, 5.0 mmol) at 0°C under a nitrogen atmosphere. The mixture was stirred for 1 h at room temperature and then quenched with aqueous saturated NH_4Cl and extracted with AcOEt. The combined organics were washed with brine, dried and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=1/2) to give **12** (1.12 g, 71%) as an orange crystal.

12: mp 228-230 °C. IR (KBr): ν 3380, 1675, 1600, 1570, 1505, cm^{-1} . ^1H NMR (300 MHz): δ 1.65 (d, 1H, $J = 11.5$ Hz), 1.85 (dd, 1H, $J = 11.5, 10.0$ Hz), 3.61-3.77 (m, 2H), 3.95 (dd, 1H, $J = 10.0, 3.0$ Hz), 6.33 (d, 1H, $J = 10.0$ Hz), 6.42 (d, 1H, $J = 10.0$ Hz), 6.69 (brs, 1H), 6.91-6.97 (m, 2H), 7.58 (t, 1H, $J = 6.5$ Hz), 7.69 (t, 1H, $J = 6.5$ Hz), 7.99 (d, 1H, $J = 8.5$ Hz), 8.02 (d, 1H, $J = 8.0$ Hz). ^{13}C NMR (68 MHz): δ 36.5, 40.3, 49.6, 65.0, 109.8, 126.0, 126.3, 127.2, 128.6, 129.8, 132.0, 133.3, 135.1, 144.9, 150.6, 155.6, 179.5, 180.3, 185.5. HR-FABMS calcd for $\text{C}_{19}\text{H}_{16}\text{NO}_4$ ($\text{M}+\text{H}^+$); 322.1079, found 322.1079.

1,2,3,4,5,10-Hexahydrobenzo[6,7-*g*]quinoline-5,10-dione-2-methoxy-4-spiro-4'-cyclohexa-2',5'-dien-1'-one (10).

To a stirred solution of **12** (81.3 mg, 0.253 mmol) in anhydrous CH₂Cl₂ (8.0 mL) – MeOH (4.0 mL) was added Pb(OAc)₄ (448.7 mg, 1.01 mmol) at room temperature under a nitrogen atmosphere. The mixture was stirred for 5 h and then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=1/1) to give **10** (49.5 mg, 61%) as a yellow solid.

1,2,3,4,5,10-Hexahydrobenzo[6,7-*g*]quinoline-5,10-dione-2-acetylthio-4-spiro4'-cyclohexa-2',5'-dien-1'-one (9a).

To a stirred solution of **10** (50.0 mg, 0.156 mmol) in THF (3.0 mL) was added potassium thioacetate (53.3 mg, 0.468 mmol) and BF₃·Et₂O (0.06 mL, 0.468 mmol) sequentially at –78°C under a nitrogen atmosphere. The reaction mixture was warmed from –78°C to 4°C by stirring for 24 h in a cooled environment (4°C). The reaction was quenched by the addition of solid NaHCO₃, and then the mixture was filtered. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography (*n*-hexane/AcOEt=2:1) to give **9a** (44.3 mg, 78%) as an orange solid.

9a: mp 149-152 °C (from AcOEt). IR (KBr): ν 1660, 1605, 1575, 1505 cm⁻¹. ¹H NMR (300 MHz): δ 2.03 (dd, 1H, *J* = 14.0, 5.0 Hz), 2.42 (s, 3H), 2.43 (dd, 1H, *J* = 14.0, 5.0 Hz), 5.59-5.63 (m, 1H), 6.38 (d, 1H, *J* = 9.9 Hz), 6.40 (d, 1H, *J* = 9.9 Hz), 6.86 (br s, 1H), 6.89 (dd, 1H, *J* = 10.8, 3.0 Hz), 7.09 (dd, 1H, *J* = 10.8, 3.0 Hz), 7.63 (t, 1H, *J* = 7.0 Hz), 7.70 (t, 1H, *J* = 7.0 Hz), 7.99 (d, 1H, *J* = 9.0 Hz), 8.02 (d, 1H, *J* = 8.0 Hz). ¹³C NMR (75 MHz): δ 30.9, 38.4, 39.7, 52.6, 110.8, 126.2, 126.5, 128.2, 128.5, 129.8, 132.4, 133.0, 135.2, 142.8, 151.6, 152.8, 179.9, 180.0, 185.2, 195.2. HRMS calcd for C₂₀H₁₃NO₄S (M⁺) 365.0722, found 365.0711.

1,2,3,4,5,10-Hexahydrobenzo[6,7-*g*]quinoline-5,10-dione-2-sulfanyl-3'-4-spiro-4'-cyclohexa-5'-en-1'-one (4).

To a stirred solution of **9a** (44.3 mg, 0.121 mmol) in EtOH (10 mL) was added 2M NH₃/EtOH solution (0.61 mL, 1.21 mmol) at room temperature. The reaction mixture was stirred for 12h, then concentrated *in vacuo*. The residue was purified by column chromatography (*n*-hexane/AcOEt=2:1) to give **4** (20.0 mg, 51%) as an orange solid.

4: mp 255-257 °C (from AcOEt). IR (KBr): ν 1680, 1675, 1595, 1565, 1495 cm^{-1} . ^1H NMR (300 MHz): δ 2.61-2.83 (m, 4H), 4.60 (dd, $J = 12.0, 7.5$ Hz, 1H), 5.29-5.33 (m, 1H), 6.19 (d, $J = 10.5$ Hz, 1H), 6.49 (br s, 1H), 7.05 (d, $J = 10.5$ Hz, 1H), 7.64 (t, $J = 8.0$ Hz, 1H), 7.75 (t, $J = 8.0$ Hz, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): δ 39.4, 45.3, 46.8, 55.7, 59.5, 118.8, 124.9, 125.4, 125.7, 129.8, 132.4, 133.0, 135.0, 144.9, 154.9, 178.4, 180.6, 195.7. UV/Vis (MeOH): $\lambda_{\text{max}}(\epsilon) = 473$ (1300), 270 (10900), 245 nm (10000). HRMS calcd for $\text{C}_{18}\text{H}_{13}\text{NO}_3\text{S}$ (M^+) 323.0616, found 323.0621.

1,2,3,4,5,10-Hexahydrobenzo[6,7-g]quinoline-5,10-dione-2-(4-methoxybenzyl-sulfanyl)-4-spiro-4'-cyclohexa-2',5'-dien-1'-one (9b).

To a stirred solution of **10** (15.7 mg, 0.0489 mmol) in THF (1.5 mL) was added *p*-methoxybenzylthiol (MeOBnSH) (6.8 μL , 0.0489 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (6.2 μL , 0.0489 mmol) sequentially at -78°C under a nitrogen atmosphere. The reaction mixture was warmed from -78°C to 4°C by stirring for 24 h in a cooled environment (4°C). The reaction was quenched by the addition of solid NaHCO_3 , and the mixture was filtered. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography (*n*-hexane/AcOEt=2:1) to give **9b** (17.2 mg, 80%) as a red solid.

9b: mp 180-182 °C (from AcOEt). IR (KBr): ν 3348, 1659, 1605, 1574, 1514, 1504 cm^{-1} . ^1H NMR (300 MHz): δ 2.04 (d, 2H, $J = 6.5$ Hz), 3.80 (s, 3H), 3.87 (s, 2H), 4.60 (td, 1H, $J = 6.5, 2.0$), 6.16 (br s, 1H), 6.32 (dd, 1H, $J = 10.0, 2.0$ Hz), 6.37 (dd, 1H, $J = 10.0, 2.0$ Hz), 6.76 (dd, 1H, $J = 10.0, 3.0$ Hz), 6.88 (d, 2H, $J = 8.5$ Hz), 7.09 (dd, 1H, $J = 10.0, 3.0$ Hz), 7.25 (d, 2H, $J = 8.5$ Hz), 7.58 (td, 1H, $J = 8.0, 1.5$ Hz), 7.68 (td, 1H, $J = 7.5, 1.5$ Hz), 7.97 (dd, 1H, $J = 7.5, 1.5$ Hz), 7.99 (dd, 1H, $J = 7.5, 1.5$ Hz), ^{13}C NMR (75 MHz): δ 30.9, 38.4, 39.7, 52.6, 110.8, 126.2, 126.5, 128.2, 128.5, 129.8, 132.4, 133.0, 135.2, 142.8, 151.6, 152.8, 179.9, 180.0, 185.2, 195.2. HRMS calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_4\text{S}$ (M^+) 443.1191, found 443.1173.

1,2,3,4,5,10-Hexahydrobenzo[6,7-g]quinoline-5,10-dione-2-sulfanyl-3'-4-spiro-4'-cyclohexa-5'-en-1'-one (4).

To a stirred solution of **9b** (25.6 mg, 0.0577 mmol) in CH₂Cl₂ (2.0 mL) was added 30% HBr-AcOH (0.05 mL) at -78°C under a nitrogen atmosphere. The reaction mixture was warmed from -78°C to 4°C by stirring for 3.5 h in a cooled environment (4°C). The reaction was quenched by the addition of solid NaHCO₃, and then the mixture was filtered. The filtrate was concentrated *in vacuo* and the residue was purified by preparative TLC (*n*-hexane/AcOEt=1:1) to give **4** (7.7 mg, 41%) as a red solid.

3-(3-Bromo-4-hydroxyphenyl)-2-(tritylamino)propionic acid methyl ester (15).

To a solution of **6•HCl** (511 mg, 2.21 mmol) in DMF (20 mL) was added triethylamine (0.62 mL, 4.44 mmol) and tritylchloride (617 mg, 2.21 mmol) sequentially at 0°C. The reaction mixture was stirred at room temperature for 3 h. The mixture was then quenched with water and diluted with AcOEt. The layers were separated, and the aqueous layer was extracted twice with AcOEt. The combined organics were washed with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=3/1) to give tritylated tyrosine methyl ester (1.003 g, quant.) as a colorless amorphous.

IR (KBr): ν 3345, 1715, 1615, 1595, 1515, 1445 cm⁻¹. ¹H NMR (300 MHz): δ 2.59 (d, 1H, *J* = 10.8 Hz), 2.88 (dd, 2H, *J* = 6.9, 4.2 Hz), 3.04 (s, 3H), 3.50 (dt, 1H, *J* = 10.8, 6.9 Hz), 4.78 (s, 1H), 6.76 (d, 2H, *J* = 8.4 Hz), 7.06 (d, 2H, *J* = 8.4 Hz), 7.11-7.26 (m, 9H), 7.40 (d, 6H, *J* = 7.5 Hz). ¹³C NMR (75 MHz): δ 41.4, 51.4, 58.4, 70.9, 115.1, 126.3, 127.7, 128.7, 129.2, 130.8, 145.8, 154.5, 175.3. HR-FABMS calcd for C₂₉H₂₈NO₃ (M+H⁺); 438.2069, found 438.2073. Anal. calcd. for C₂₉H₂₇NO₃•0.4H₂O: C 79.61, H 6.22, N 3.20; found C 78.14, H 6.52, N 3.02.

To a stirred solution of tritylated tyrosine methyl ester (3.28 g, 7.5 mmol) in DMF (40 mL) was added dropwise slowly a solution of NBS (1.34 g, 7.5 mmol) in DMF at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 2.5 h. The mixture was then quenched with water and diluted with Et₂O. The layers were separated, and the aqueous layer was extracted twice with Et₂O. The combined organics

were washed twice with water and once with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=4/1) to give **15** (2.546 g, 65%) as a colorless amorphous.

15: IR (KBr): ν 3500, 3340, 1730, 1605, 1595, 1495, 1445 cm^{-1} . ^1H NMR (300 MHz): δ 2.57 (d, 1H, J = 10.8 Hz), 2.85 (d, 2H, J = 6.6 Hz), 3.06 (s, 3H), 3.49-3.52 (m, 1H), 5.43 (s, 1H), 6.95 (d, 1H, J = 8.4 Hz), 7.04 (dd, 1H, J = 8.4, 1.8 Hz), 7.12-7.31 (m, 9H), 7.32 (d, 1H, J = 1.8 Hz), 7.39 (d, 6H, J = 6.9 Hz). ^{13}C NMR (75 MHz): δ 40.9, 51.4, 58.0, 70.9, 109.7, 115.7, 126.4, 127.8, 128.7, 130.5, 131.0, 133.1, 145.7, 151.1, 174.7. HR-FABMS calcd for $\text{C}_{29}\text{H}_{27}\text{BrNO}_3$ ($\text{M}+\text{H}^+$); 516.1174, found 516.1166. Anal. calcd. for $\text{C}_{29}\text{H}_{26}\text{BrNO}_3 \cdot 0.2\text{H}_2\text{O}$: C 67.15, H 5.09, N 2.70, Br 15.40; found C 66.90, H 5.21, N 2.46, Br 15.08.

3-(3-Bromo-4-hydroxy-phenyl)-2-(8-oxo-1,3,4,8-tetrahydropyrrolo[4,3,2-*de*]quinolin-7-ylamino) propionic acid methyl ester (17**).**

0.1M MeOH solution of HCl (0.9 mL) was added to **15** (18.1 mg, 0.0350 mmol) at room temperature under a nitrogen atmosphere and the mixture was stirred for 30 min. The above mixture was added dropwise to a stirred solution of 7-methoxy-3,4-dihydro-1H-pyrrolo[4,3,2-*de*]quinolin-8-one (**16a**) (7.0 mg, 0.0346 mmol) in MeOH (0.5 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred for 18 h under the same conditions and was then concentrated *in vacuo*. The residue was purified by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{CF}_3\text{CO}_2\text{H}$ =100:5:0.1) to give **17•TFA** (7.3 mg, 37%) as a red amorphous.

17•TFA: ^1H NMR (270 MHz, CD_3OD): δ 2.95 (t, 2H, J = 7.5 Hz), 3.08 (dd, 1H, J = 14.0, 8.0 Hz), 3.26 (dd, 1H, J = 14.0, 5.0 Hz), 3.77 (s, 3H), 3.86 (t, 2H, J = 7.5 Hz), 4.56 (dd, 1H, J = 8.0, 5.5 Hz), 5.35 (br s, 1H), 6.79 (d, 1H, J = 8.5 Hz), 7.00 (dd, 1H, J = 8.5, 2.0 Hz), 7.14 (s, 1H), 7.30 (d, 1H, J = 2.0 Hz). HR-FABMS calcd for $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_4\text{Br}$ ($\text{M}+\text{H}^+$); 444.0559, found 444.0532.

[2-[3-Bromo-4-(*tert*-butyldimethylsilyloxy)phenyl]-1-(*tert*-butyldimethylsilyloxy-methyl)ethyl]tritylamine (19a**).**

To a stirred solution of **15** (1.3749 g, 2.66 mmol) in CH₂Cl₂ (50 mL) was added dropwise slowly a solution of diisobutylaluminum hydride (DIBAH) 1.0 M solution in hexane (8.6 mL, 8.6 mmol) at –78°C under a nitrogen atmosphere. The reaction mixture was stirred for 5 h at –78°C to room temperature. The mixture was then quenched with water at 0°C and filtered through celite. The filtrate was washed with aqueous saturated NaHCO₃ and then with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=2/1) to give monobrominated *N*-tritylated (*L*)-tyrosinol (1.246 g, 96%) as a colorless amorphous.

IR (KBr): ν 3505, 3330, 1595, 1495, 1445 cm⁻¹. ¹H NMR (300 MHz): δ 1.96 (br s, 1H), 2.15 (dd, 1H, *J* = 13.2, 4.8 Hz), 2.42 (dd, 1H, *J* = 13.2, 9.6 Hz), 2.70-2.74 (m, 1H), 2.97 (dd, 1H, *J* = 10.8, 4.2 Hz), 3.10 (dd, 1H, *J* = 10.8, 2.7 Hz), 6.76 (dd, 1H, *J* = 8.4, 1.8 Hz), 6.81 (d, 1H, *J* = 8.4 Hz), 6.98 (d, 1H, *J* = 1.8 Hz), 7.17-7.31 (m, 9H), 7.54 (d, 6H, *J* = 7.5 Hz). ¹³C NMR (75 MHz): δ 37.8, 55.2, 62.3, 71.3, 109.9, 115.7, 126.6, 127.9, 128.6, 130.1, 132.6, 132.7, 146.4, 150.6. HR-FABMS calcd for C₂₈H₂₇BrNO₂ (*M*+H⁺); 488.1225, found 488.1257.

To a stirred solution of monobrominated *N*-tritylated (*L*)-tyrosinol (1.246 g, 2.55 mmol) in CH₂Cl₂ (20 mL) was added DBU (1.90 mL, 12.7 mmol) and TBSCl (1.166 g, 7.74 mmol) sequentially at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 2.5 h at 0°C. The mixture was then quenched with aqueous saturated NaHCO₃ and extracted with CH₂Cl₂. The combined organics were washed with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=20/1) to give **19a** (1.583 g, 87%) as a colorless oil.

19a: IR (KBr): ν 3320, 1600, 1495, 1470, 1460 cm⁻¹. ¹H NMR (300 MHz): δ –0.13 (s, 3H), –0.11 (s, 3H), 0.20 (s, 6H), 0.85 (s, 9H), 1.02 (s, 9H), 2.14 (d, 1H, *J* = 6.3 Hz), 2.46-2.61 (m, 3H), 2.68 (br s, 1H), 2.90 (dd, 1H, *J* = 9.6, 3.0 Hz), 6.69 (d, 1H, *J* = 8.4 Hz), 6.80 (dd, 1H, *J* = 8.4, 1.8 Hz), 7.18 (d, 1H, *J* = 1.8 Hz), 7.15-7.29 (m, 9H), 7.56 (d, 6H, *J* = 7.5 Hz). ¹³C NMR (75 MHz): δ –5.5, –5.4, –4.3, 18.1, 18.3, 25.7, 25.9, 37.7, 55.2, 62.3, 71.1, 114.8, 119.7, 126.3, 127.8, 128.7, 129.3, 133.9, 134.3, 147.2, 150.6.

HR-FABMS calcd for $C_{40}H_{33}BrNO_2Si_2$ ($M+H^+$); 716.2955, found 716.2942. Anal. calcd. for $C_{40}H_{34}BrNO_2Si_2$: C 67.01, H 7.59, N 1.95, Br 11.15; found C 67.02, H 7.58, N 1.77, Br 10.89.

[2-[3-bromo-4-hydroxyphenyl]-1-(*tert*-butyldimethylsilyloxymethyl)ethyl] tritylamine (19b).

To a stirred solution of **19a** (1.577 g, 2.20 mmol) in THF (35 mL) was added TBAF (2.2 mL (1.0 M solution in THF), 2.20 mmol) at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 0.5 h at 0°C. The mixture was then quenched with aqueous saturated NH_4Cl and extracted with AcOEt. The combined organics were washed with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=10/1) to give **19b** (1.330 g, quant.) as a colorless oil.

19b: IR (KBr): ν 3520, 3325, 1595, 1495, 1470, 1450 cm^{-1} . 1H NMR (300 MHz): δ – 0.13 (s, 3H), –0.11 (s, 3H), 0.85 (s, 9H), 2.10 (br s, 1H), 2.47-2.61 (m, 3H), 2.69 (br s, 1H), 2.88 (dd, 1H, J = 9.6, 3.0 Hz), 5.40 (br s, 1H), 6.85-6.86 (m, 2H), 7.13 (d, 1H, J = 1.8 Hz), 7.12-7.29 (m, 9H), 7.56 (d, 6H, J = 7.5 Hz). ^{13}C NMR (75 MHz): δ –5.5, –5.4, 18.1, 25.9, 37.6, 55.1, 62.3, 71.1, 109.7, 115.5, 126.3, 127.8, 128.7, 130.3, 132.9, 133.3, 147.1, 150.3. HR-FABMS calcd for $C_{34}H_{41}BrNO_2Si$ ($M+H^+$); 602.2090, found 602.2075. Anal. calcd. for $C_{34}H_{41}BrNO_2Si$: C 67.76, H 6.69, N 2.32, Br 13.26; found C 68.11, H 6.79, N 2.29, Br 12.64.

7-Methoxy-1-(toluene-4-sulfonyl)-3,4-dihydro-1H-pyrrolo[4,3,2-*de*]quinolin-8-one (16b).

To a stirred solution of 3-(2-azidoethyl)-6,7-dimethoxy-1-[(4-methylphenyl)-sulfonyl] indole^{6b} (215.4 mg, 0.538 mmol) in $(CF_3)_2CHOH$ (15 mL)- H_2O (0.3 mL) was added drpwise trimethylsilyl trifluoromethane sulfonate (0.23 mL, 1.271 mmol) followed by PIFA (277.4 mg, 0.645 mmol) at 0°C under a nitrogen atmosphere. After stirring for 1.5 h at 0 °C, the mixture was quenched with saturated aqueous $NaHCO_3$, stirred for 15min, and then extracted with CH_2Cl_2 . The combined organics were washed with brine,

dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (CH₂Cl₂/MeOH/Et₃N=100:5:0.1) to give **16b** (144.9 mg, 76%) as a yellow solid.

IR (KBr): ν 1670, 1620, 1595, 1580, 1535 cm⁻¹. ¹H NMR (CDCl₃): δ 2.40 (s, 3H), 2.78 (t, 2H, *J* = 7.6 Hz), 3.78 (s, 3H), 4.18 (t, 2H, *J* = 7.6 Hz), 6.09 (s, 1H), 7.31 (d, 2H, *J* = 8.2 Hz), 7.51 (s, 1H), 8.08 (d, 2H, *J* = 8.2 Hz). HRMS calcd for C₁₈H₁₆N₂O₄S (M⁺) 356.0831, found 356.0825. This compound gradually decomposed during ¹³C NMR measurement due to its unstability.

7-[2-(3-Bromo-4-hydroxyphenyl)-1-(*tert*-butyldimethylsilyloxymethyl)-ethylamino]-1-(toluene-4-sulfonyl)-3,4-dihydro-1*H*-pyrrolo[4,3,2-*de*]quinolin-8-one (20a).

0.1N MeOH solution of HCl (5.2 mL) was added to **19b** (312.4 mg, 0.518 mmol) at room temperature under a nitrogen atmosphere and the mixture was stirred for 30 min. The above mixture was added dropwise to a stirred solution of **16b** (144.9 mg, 0.407 mmol) in MeOH (1.0 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred for 16 h under the same conditions and was then concentrated *in vacuo*. The residue was purified by flash chromatography (CH₂Cl₂/MeOH/Et₃N=100:5:0.1) to give **20a** (149.8 mg, 54%) as a red amorphous solid.

20a: IR (KBr): ν 3370, 1665, 1610, 1580, 1550, 1535, 1495, 1460, 1445, 1380 cm⁻¹. ¹H NMR (500 MHz, CD₃OD): δ 0.01 (s, 6H), 0.89 (s, 9H), 2.41 (s, 3H), 2.71-2.81 (m, 4H), 3.58-3.61 (m, 2H), 3.66 (dd, 1H, *J* = 10.5, 4.5 Hz), 3.97 (br s, 2H), 5.49 (br s, 1H), 6.76 (d, 1H, *J* = 8.5 Hz), 6.99 (dd, 1H, *J* = 8.5, 2.0 Hz), 7.28 (d, 1H, *J* = 2.0 Hz), 7.39 (d, 2H, *J* = 8.5 Hz), 7.66 (br s, 1H), 8.00 (d, 2H, *J* = 8.5 Hz). ¹³C NMR (125 MHz, CD₃OD, as its HCl salt): δ -5.74, 19.0, 21.8, 26.3, 36.5, 43.5, 49.9, 59.9, 63.5, 86.8, 110.7, 117.4, 119.9, 124.2, 129.0, 130.1, 130.2, 130.7, 131.1, 131.2, 134.7, 134.9, 148.6, 154.2, 157.8, 166.9. HR-FABMS calcd for C₃₂H₃₉BrN₃O₃SSi (M+H⁺); 684.1563, found 684.1586.

**5-(Toluene-4-sulfonyl)-3,5,7,8,9,10-hexahydro-2*H*-1,5,7-triaza-
acephenanthrylen-6-one-8-(*tert*-butyldimethylsilyloxymethyl)-10-spiro-4'-2'-
bromocyclohexa-2',5'-dien-1'-one (21).**

To a stirred solution of **20a** (110.7 mg, 0.162 mmol) in CF₃CH₂OH (10 mL) was added MK10 (50 mg) and PIFA (90.4 mg, 0.210 mmol) sequentially at room temperature. The mixture was stirred for 30 min. under the same conditions and then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt/Et₃N= 100:50:0.1) to afford two diastereomers **21a** (30 mg, 27%) and **21'a** (20 mg, 18%) respectively as a red amorphous solid.

21a (less polar): IR (KBr): ν 3390, 1660, 1595, 1575, 1525, 1460, 1435, 1380 cm⁻¹. ¹H NMR (500 MHz): δ 0.08 (s, 3H), 0.10 (s, 3H), 0.92 (s, 9H), 1.57 (d, 1H, *J* = 13.5 Hz), 1.72 (t, 1H, *J* = 11.5 Hz), 2.40 (s, 3H), 2.60 (t, 2H, *J* = 8.0 Hz), 3.49-3.52 (m, 2H), 3.71-3.72 (m, 1H), 3.83 (dt, 1H, *J* = 8.5, 17.5 Hz), 4.09 (dt, 1H, *J* = 7.0, 19.5 Hz), 6.07 (br s, 1H), 6.27 (d, 1H, *J* = 9.5 Hz), 6.96 (dd, 1H, *J* = 9.5, 2.5 Hz), 7.20 (d, 1H, *J* = 3.0 Hz), 7.30 (d, 2H, *J* = 8.5 Hz), 7.43 (s, 1H), 8.02 (d, 2H, *J* = 8.5 Hz). ¹³C NMR (125 MHz): δ -5.4, 17.5, 18.3, 21.7, 25.9, 36.6, 43.9, 49.6, 66.1, 104.2, 118.5, 121.9, 125.5, 125.9, 126.1, 128.7, 129.7, 134.7, 142.0, 145.7, 152.2, 152.7, 157.1, 168.4, 179.0. UV/Vis (CH₂Cl₂): $\lambda_{\max}(\epsilon)$ = 487(2000), 330(11300), 234 nm (27800). HR-FABMS calcd for C₃₂H₃₇BrN₃O₃SSi (*M*+H⁺); 682.1407, found 682.1392. [α]_D^{23.0} +149.8° (c 0.46, CHCl₃).

21'a (polar): IR (KBr): ν 3390, 1660, 1595, 1575, 1525, 1460, 1435, 1380 cm⁻¹. ¹H NMR (300 MHz): δ 0.10 (s, 3H), 0.12 (s, 3H), 0.95 (s, 9H), 1.60 (m, 1H), 1.73 (t, 1H, *J* = 12.0 Hz), 2.43 (s, 3H), 2.61 (t, 2H, *J* = 7.0 Hz), 3.48-3.60 (m, 2H), 3.74-3.86 (m, 2H), 4.07 (dt, 1H, *J* = 17.7, 6.5 Hz), 6.12 (br s, 1H), 6.33 (d, 1H, *J* = 9.9 Hz), 6.91 (dd, 1H, *J* = 9.9, 2.7 Hz), 7.32 (d, 2H, *J* = 8.1 Hz), 7.42 (d, 1H, *J* = 2.4 Hz), 7.45 (s, 1H), 8.03 (d, 2H, *J* = 8.4 Hz). ¹³C NMR (125 MHz): δ -5.4, -5.3, 17.6, 18.4, 21.7, 25.9, 36.8, 44.0, 49.6, 66.1, 103.9, 118.6, 121.9, 123.9, 125.0, 125.6, 126.1, 128.7, 129.7, 134.7, 142.2, 145.8, 152.3, 152.8, 157.1, 168.4, 179.0. UV/Vis (CH₂Cl₂): $\lambda_{\max}(\epsilon)$ = 486(2200),

331(12200), 233 nm (26900). HR-FABMS calcd for $C_{32}H_{37}BrN_3O_3SSi$ ($M+H^+$); 682.1407, found 682.1413. $[\alpha]_D^{25.0} +107.7^\circ$ (c 0.34, $CHCl_3$).

3,5,7,8,9,10-hexahydro-2*H*-1,5,7-triaza-acephenanthrylen-6-one-8-methylene[5'] ether-10-spiro-4'-(6'-bromo)-cyclohex-2'-en-1'-one (23a).

To a stirred solution of **21a** (74.3 mg, 0.109 mmol) in CH_2Cl_2 (7 mL) was added $BF_3 \cdot Et_2O$ (0.28 mL, 2.18 mmol) at $0^\circ C$ under a nitrogen atmosphere. The reaction mixture was stirred for 4 h at $0^\circ C$ then to room temperature. The mixture was quenched with $NaHCO_3$, filtered and then concentrated *in vacuo*. The residue was purified by flash chromatography ($CH_2Cl_2/MeOH=20/1$) to give **22** (54.5 mg, 88%) as a red amorphous.

22: IR (KBr): ν 3390, 1660, 1570, 1525, 1485, 1460, 1375 cm^{-1} . 1H NMR (300 MHz, $(CD_3)_2CO$): δ 1.65 (dd, 1H, $J = 13.0, 3.0$ Hz), 1.91 (t, 1H, $J = 12.0$ Hz), 2.43 (s, 3H), 2.65 (dd, 2H, $J = 8.0, 7.0$ Hz), 3.53-3.66 (m, 2H), 3.74-3.86 (m, 2H), 4.05 (dt, 1H, $J = 18.0, 7.0$ Hz), 6.17 (d, 1H, $J = 10.0$ Hz), 6.25 (br s, 1H), 7.22 (dd, 1H, $J = 10.0, 2.5$ Hz), 7.46 (d, 1H, $J = 3.0$ Hz), 7.47 (d, 2H, $J = 7.5$ Hz), 7.64 (s, 1H), 8.06 (d, 2H, $J = 8.0$ Hz). ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ 18.0, 21.6, 37.2, 45.0, 50.3, 50.4, 65.3, 105.0, 119.6, 122.2, 122.6, 126.9, 127.5, 128.2, 129.4, 130.2, 130.3, 130.7, 135.7, 143.2, 147.1, 154.1, 158.6, 169.3, 178.8. UV/Vis (CH_2Cl_2): $\lambda_{max}(\epsilon) = 486(1600), 330(10000), 230$ nm (28000). HR-FABMS calcd for $C_{26}H_{23}BrN_3O_3S$ ($M+H^+$); 568.0542, found 568.0539. $[\alpha]_D^{24.9} +182^\circ$ (c 0.133, $CHCl_3$).

To a stirred solution of **22** (24.2 mg, 0.0426 mmol) in CH_2Cl_2 (2.7 mL) was added 30% HBr-AcOH (0.04 mL) at $-78^\circ C$ under a nitrogen atmosphere. The reaction mixture was warmed from $-78^\circ C$ to $4^\circ C$ by stirring for 36 h in a cooled environment ($4^\circ C$). The mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with CH_2Cl_2 . The aqueous layer was treated with saturated aqueous $NaHCO_3$ and was extracted with CH_2Cl_2 again. The combined organics were dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt = 1:1) to afford **23a** (19.4 mg, 80%) as a red solid.

23a: mp 150°C decomp. IR (KBr): ν 3391, 2926, 2851, 1661, 1572, 1524, 1487, 1460 cm^{-1} . ^1H NMR (300 MHz): δ 1.85 (d, 1H, $J = 12.5$ Hz), 1.94 (dd, 1H, $J = 13.0$, 2.0 Hz), 2.40 (s, 3H), 2.64 (t, 2H, $J = 7.5$ Hz), 3.67 (br s, 1H), 3.69-3.87 (m, 2H), 3.83 (s, 2H), 4.12 (dt, 1H, $J = 20.0$, 6.0 Hz), 4.22 (d, 1H, $J = 12.5$ Hz), 5.06 (d, 1H, $J = 12.5$ Hz), 5.95 (br s, 1H), 6.07 (d, 1H, $J = 10.0$ Hz), 7.12 (d, 1H, $J = 10.0$ Hz), 7.31 (d, 2H, $J = 8.5$ Hz), 7.46 (s, 1H), 7.98 (d, 2H, $J = 8.5$ Hz). ^{13}C NMR (125 MHz): δ 17.8, 21.7, 28.9, 38.9, 44.3, 49.5, 52.3, 68.0, 80.2, 108.5, 118.6, 122.1, 123.0, 125.4, 126.0, 128.6, 129.8, 134.6, 143.7, 145.9, 152.5, 157.4, 168.4, 190.7. $[\alpha]_{\text{D}}^{26.2} -28.6^\circ$ (c 0.281, CHCl_3). HR-FABMS calcd for $\text{C}_{26}\text{H}_{23}\text{BrN}_3\text{O}_3\text{S}$ ($M+\text{H}^+$); 568.0541, found 568.0549.

3,5,7,8,9,10-hexahydro-2H-1,5,7-triaza-acephenanthrylen-6-one-8-methylene[5']ether-10-spiro-4'-(2'-bromo)cyclohex-2'-en-1'-one (23b).

To a stirred solution of desilylated **21'a** (9.1 mg, 0.0160 mmol) in CH_2Cl_2 (1.0 mL) was added 30% HBr-AcOH (0.015 mL) at -78°C under a nitrogen atmosphere. The reaction mixture was warmed from -78°C to 4°C by stirring for 41 h in a cooled environment (4°C). The mixture was quenched with aqueous saturated NaHCO_3 and extracted with CH_2Cl_2 . The aqueous layer was treated with saturated aqueous NaHCO_3 and was extracted with CH_2Cl_2 again. The combined organics were dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt = 1:1) to afford **23b** (5.7 mg, 63%) as a red solid.

23b: a red solid, mp 180°C decomp. IR (KBr): ν 3393, 2926, 1682, 1659, 1595, 1572, 1524, 1493, 1460 cm^{-1} . ^1H NMR (300 MHz): δ 1.83 (d, 1H, $J = 12.5$ Hz), 2.06 (d, 1H, $J = 13.5$ Hz), 2.42 (s, 3H), 2.68 (dd, 2H, $J = 8.5$, 1.5 Hz), 2.85 (dd, 1H, $J = 16.5$, 5.5 Hz), 3.03 (dd, 1H, $J = 16.5$, 13.0 Hz), 3.64 (br s, 1H), 3.74 (d, 1H, $J = 12.0$ Hz), 3.80-3.89 (m, 2H), 4.26 (dt, 1H, $J = 17.5$, 6.0 Hz), 4.34 (dd, 1H, $J = 11.5$, 5.5 Hz), 5.89 (d, 1H, $J = 4.0$ Hz), 7.33 (d, 2H, $J = 8.0$ Hz), 7.49 (s, 1H), 7.51 (s, 1H), 8.02 (d, 2H, $J = 8.5$ Hz). ^{13}C NMR (75 MHz): δ 17.8, 21.7, 27.2, 37.4, 39.2, 44.3, 49.7, 68.1, 74.4, 108.5, 118.5, 119.1, 122.0, 125.3, 125.9, 128.5, 128.6, 129.7, 129.8, 134.5, 143.3, 145.9, 152.3, 157.9,

168.4, 190.2. $[\alpha]_D^{27.2} -49.8^\circ$ (c 0.227, CHCl_3). HR-FABMS calcd for $\text{C}_{26}\text{H}_{23}\text{BrN}_3\text{O}_3\text{S}$ ($M+\text{H}^+$); 568.0542, found 568.0556.

8-Methoxy-3,5,7,9,10-hexahydro-2H-1,5,7-triazaacephenanthrylen-6-one-10-spiro-4'-cyclohexa-2'-bromo-2',5'-diene-1'-one (24).

To a stirred solution of **22** (19.9 mg, 0.0350 mmol) in CH_2Cl_2 (2 mL)-MeOH (1.0 mL) was added $\text{Pb}(\text{OAc})_4$ (31.0 mg, 0.0700 mmol) at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 1.5 h at 0°C then to room temperature. The mixture was then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt/ Et_3N = 100:100:0.1) to give **24** (15.9mg, 80%) as a diastereomeric mixture (**24a** + **24b**).

24a: (less polar): a yellow solid. IR (KBr): ν 3385, 1660, 1585, 1530, 1495, 1460, 1375 cm^{-1} . ^1H NMR (500 MHz): δ 1.92 (d, 1H, $J = 14.0$ Hz), 2.00 (dd, 1H, $J = 3.5, 14.0$ Hz), 2.41 (s, 3H), 2.62 (t, 2H, $J = 7.5$ Hz), 3.30 (s, 3H), 3.88 (dt, 1H, $J = 8.0, 18.5$ Hz), 4.09 (dt, 1H, $J = 7.5, 18.5$ Hz), 4.72 (m, 1H), 6.23 (d, 1H, $J = 10.0$ Hz), 6.49 (br s, 1H), 7.20 (d, 1H, $J = 3.0$ Hz), 7.27 (dd, 1H, $J = 2.5, 10.0$ Hz), 7.32 (d, 2H, $J = 8.5$ Hz), 7.46 (s, 1H), 8.01 (d, 2H, $J = 8.5$ Hz). ^{13}C NMR (125 MHz): δ 17.4, 21.7, 37.7, 42.9, 49.9, 54.5, 79.3, 106.9, 118.5, 121.9, 122.7, 125.1, 125.4, 126.3, 128.6, 129.8, 134.6, 139.2, 145.9, 152.9, 153.4, 155.8, 168.3, 179.3. UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}(\epsilon) = 327(11000), 229$ nm (28000). HR-FABMS calcd for $\text{C}_{26}\text{H}_{23}\text{BrN}_3\text{O}_3\text{S}$ ($M+\text{H}^+$); 568.0542, found 568.0551.

24b: (polar): a yellow solid. IR (KBr): ν 3385, 1660, 1585, 1525, 1490, 1460, 1375 cm^{-1} . ^1H NMR (500 MHz): δ 1.91 (d, 1H, $J = 13.0$ Hz), 1.98 (dd, 1H, $J = 3.0, 14.0$ Hz), 2.41 (s, 3H), 2.56-2.63 (m, 2H), 3.13 (s, 3H), 3.84 (dt, 1H, $J = 8.0, 19.0$ Hz), 4.07 (dt, 1H, $J = 6.5, 19.5$ Hz), 4.72 (m, 1H), 6.32 (d, 1H, $J = 9.5$ Hz), 6.51 (br s, 1H), 6.81 (dd, 1H, $J = 3.0, 10.0$ Hz), 7.32 (d, 2H, $J = 8.5$ Hz), 7.46 (s, 1H), 7.69 (d, 1H, $J = 3.0$ Hz), 8.00 (d, 2H, $J = 8.5$ Hz). ^{13}C NMR (125 MHz): δ 17.5, 21.7, 37.9, 42.8, 49.8, 54.5, 79.4, 106.8, 118.5, 121.7, 122.9, 125.4, 125.5, 126.3, 128.6, 129.8, 134.5, 139.4, 145.9, 153.0, 153.8, 155.7, 168.4, 179.2. UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}(\epsilon) = 329(12000), 232$ nm (26000). HR-FABMS calcd for $\text{C}_{26}\text{H}_{23}\text{BrN}_3\text{O}_3\text{S}$ ($M+\text{H}^+$); 568.0542, found 568.0526.

25b: unstable diastereomeric mixture (**25b-I** + **25b-II**). HR-FABMS Calcd for $C_{33}H_{29}BrN_3O_3S_2$ ($M+H^+$); 690.0732, found 690.0715.

13-(Toluene-4-sulfonyl)-discorhabdin A (**5-(Toluene-4-sulfonyl)-3,5,7,8,9,10-hexahydro-2H-1,5,7-triaza-acephenanthrylen-6-one-8-sulfanyl[5']-10-spiro-4'-(2'-bromo)-cyclohex-2'-en-1'-one**) (**26**).

To a stirred solution of **24** (diastereomeric mixture: **24a** + **24b**) (25.0 mg, 0.044 mmol) in CH_2Cl_2 (1.5 mL) was added 4-methoxybenzylthiol (7.4 μ L, 0.053 mmol) followed by dropwise 30% HBr-AcOH (0.038 mL) at $-78^\circ C$ under a nitrogen atmosphere. The reaction mixture was warmed from $-78^\circ C$ to $4^\circ C$ by stirring for 38 h in a cooled environment ($4^\circ C$). The mixture was quenched with 40% aqueous $MeNH_2$, diluted with CH_2Cl_2 , acidified with 10% aqueous HCl, and then extracted with CH_2Cl_2 . The aqueous layer was treated with saturated aqueous $NaHCO_3$ and was extracted with CH_2Cl_2 again. The combined organics were dried, and concentrated *in vacuo*. The residue was purified by preparative TLC ($CH_2Cl_2/MeOH=30/1$) to produce **26** (5.4 mg, 22%, >99%*ee* (**26**•HCl salt by HPLC (DAICEL CHIRALCEL OD, flow rate 1.0 mL/min, *n*-hexane/*i*-PrOH 95/5, $20^\circ C$)), 5-(toluene-4-sulfonyl)-3,5,7,8,9,10-hexahydro-2H-1,5,7-triaza-acephenanthrylen-6-one-8-sulfanyl-[5']-10-spiro-4'-cyclohex-2'-en-1'-one (**28**) (6.9 mg, 32%), and a trace amount of 5-(toluene-4-sulfonyl)-3,5,7,8,9,10-hexahydro-2H-1,5,7-triaza-acephenanthrylen-6-one-8-sulfanyl[3']-10-spiro-4'-(2'-bromo)-cyclohex-5'-en-1'-one (**27**) respectively.

26: a red solid. mp $>300^\circ C$. IR (KBr): ν 3365, 1680, 1660, 1610, 1595, 1565, 1525, 1455, 1375 cm^{-1} . 1H NMR (300 MHz): δ 2.42 (s, 3H), 2.61-2.77 (m, 4H), 2.80-2.85 (m, 2H), 3.88 (dt, 1H, $J = 9.0, 18.5$ Hz), 4.29 (dt, 1H, $J = 18.5, 6.0$ Hz), 4.62 (dd, 1H, $J = 8.0, 11.5$ Hz), 5.28 (t, 1H, $J = 4.0$ Hz), 5.93 (s, 1H), 7.33 (d, 2H, $J = 8.5$ Hz), 7.43 (s, 1H), 7.49 (s, 1H), 8.02 (d, 2H, $J = 8.5$ Hz). ^{13}C NMR (125 MHz): δ 17.7, 21.7, 39.9, 45.5, 50.0, 50.0, 55.9, 61.3, 116.2, 118.4, 119.6, 121.9, 125.1, 126.1, 128.7, 129.8, 134.5, 140.6, 146.0, 152.8, 154.8, 168.3, 188.0. UV/Vis ($CHCl_3$): $\lambda_{max}(\epsilon) = 483(1400)$,

326 (12200), 265 (14400), 242 nm (18200). $[\alpha]_D^{24.9} -72.7^\circ$ (c 0.0525, CHCl₃). HR-FABMS calcd for C₂₅H₂₁BrN₃O₄S₂ (M+H⁺); 570.0157, found 570.0171.

27: a red solid. mp >300°C. IR (KBr): ν 3375, 1690, 1660, 1615, 1595, 1560, 1525, 1480, 1460, 1380 cm⁻¹. ¹H NMR (300 MHz): δ 2.42 (s, 3H), 2.63-2.71 (m, 4H), 3.77-3.87 (m, 1H), 4.23 (dt, 1H, $J = 17.5, 6.5$ Hz), 4.77-4.86 (m, 2H), 5.30 (br s, 1H), 5.99 (d, 1H, $J = 4.5$ Hz), 6.10 (d, 1H, $J = 10.0$ Hz), 7.07 (d, 1H, $J = 10.5$ Hz), 7.33 (d, 2H, $J = 8.5$ Hz), 7.49 (s, 1H), 8.01 (d, 2H, $J = 8.5$ Hz). ¹³C NMR (75 MHz): δ 17.7, 21.7, 41.5, 49.5, 49.6, 60.6, 61.4, 66.6, 115.0, 118.4, 121.8, 123.5, 125.2, 126.0, 128.7, 129.8, 134.4, 140.5, 146.0, 152.9, 154.5, 168.2, 188.6. UV/Vis (CH₂Cl₂): $\lambda_{\max}$ (ϵ) = 489 (1500), 327 (13300), 237 nm (27300). $[\alpha]_D^{24.3} +55.2^\circ$ (c 0.0755, CHCl₃). HR-FABMS calcd for C₂₅H₂₁BrN₃O₄S₂ (M+H⁺); 570.0157, found 570.0142.

28: a red solid. mp >300°C. ¹H NMR (300 MHz): δ 2.42 (s, 3H), 2.57-2.78 (m, 6H), 3.75-3.88 (m, 1H), 4.26 (dt, 1H, $J = 17.5, 6.5$ Hz), 4.60 (dd, 1H, $J = 11.5, 7.0$ Hz), 5.26 (t, 1H, $J = 3.0$ Hz), 5.90 (d, 1H, $J = 4.5$ Hz), 5.99 (d, 1H, $J = 10.0$ Hz), 7.03 (d, 1H, $J = 10.0$ Hz), 7.33 (d, 2H, $J = 8.0$ Hz), 7.49 (s, 1H), 8.03 (d, 2H, $J = 8.5$ Hz). ¹³C NMR (75 MHz): δ 17.7, 21.7, 41.0, 45.9, 47.3, 49.7, 56.3, 61.0, 116.9, 118.4, 121.9, 125.4, 125.8, 128.7, 129.8, 134.5, 140.8, 145.9, 153.1, 154.6, 168.5, 196.2. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 479 (1500), 327 (13000), 243 nm (22500). $[\alpha]_D^{22.4} +134^\circ$ (c 0.146, CHCl₃). HR-FABMS calcd for C₂₅H₂₂N₃O₄S₂ (M+H⁺); 492.1052, found 492.1049.

Discorhabdin A (**1**).

To a stirred solution of **15** (3.9 mg, 0.00684 mmol) in THF (0.7 mL) was added 0.2 M NaOMe/MeOH (0.09 mL) at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 5 h at 0 °C. The mixture was purified by preparative TLC (CH₂Cl₂/MeOH=10/1) to give **1** (1.7 mg, 61%) as its free base. 0.1 N HCl/MeOH (0.05 mL) was added dropwise to a stirred solution of **1** in MeOH (0.5 mL) at room temperature, and the mixture was concentrated *in vacuo* to give HCl salt of **1** (**1•HCl**), which is more stable than its free base form, as a green solid.

1•HCl: IR (KBr): ν 3650-2400, 1680, 1610, 1580, 1525, 1435, 1410, 1390 cm^{-1} . ^1H NMR (300 MHz, CD_3OD): δ 2.60 (dd, 1H, $J = 12.5, 1.0$ Hz), 2.88 (dd, 1H, $J = 17.0, 6.5$ Hz), 2.94-3.02 (m, 3H), 3.07 (dd, 1H, $J = 17.0, 12.0$ Hz), 3.80 (dt, 1H, $J = 13.5, 5.0$ Hz), 3.93 (dt, 1H, $J = 13.5, 6.5$ Hz), 4.51 (dd, 1H, $J = 12.0, 6.5$ Hz), 5.37 (dd, 1H, $J = 4.0, 1.0$ Hz), 7.19 (s, 1H), 7.57 (s, 1H). ^{13}C NMR (125 MHz, $[\text{D}_6]\text{DMSO}$): δ 18.4, 40.8, 44.2, 44.8, 49.9, 54.2, 59.1, 104.2, 120.3, 123.6, 123.7, 126.1, 127.6, 148.3, 150.7, 154.1, 166.3, 187.2. UV/Vis (MeOH): $\lambda_{\text{max}}(\epsilon) = 558(800), 349(7000), 249 \text{ nm}(17100)$. $[\alpha]_{\text{D}}^{24.4} +388^\circ$ (c 0.06, CD_3OD). ($[\alpha]_{\text{D}} +400^\circ$ (c 0.05, CH_3OH) 1c); HR-FABMS calcd for $\text{C}_{18}\text{H}_{15}\text{BrN}_3\text{O}_2\text{S}$ ($M+\text{H}^+$); 416.0068, found 416.0066.

7-[2-(3-Bromo-4-*tert*-butyldimethylsilyloxyphenyl)-1-(*tert*-butyldimethylsilyloxymethyl)ethylamino]-1-(toluene-4-sulfonyl)-3,4-dihydro-1*H*-pyrrolo[4,3,2-*de*]quinolin-8-one (20e).

0.1N MeOH solution of HCl (2.5 mL) was added to **19a** (118.1 mg, 0.165 mmol) at room temperature under a nitrogen atmosphere and the mixture was stirred for 30 min. The above mixture was added dropwise to a stirred solution of **16b** (58.7 mg, 0.165 mmol) in MeOH (4.0 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred for 48 h under the same conditions and was then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane /AcOEt/Et₃N=100:100:0.1) to give **20e** (88.7 mg, 67%) as a red oil.

20e: IR (KBr): ν 2930, 2953, 2856, 1661, 1578, 1531, 1493 cm^{-1} . ^1H NMR (500 MHz, CD_3OD): δ 0.02 (s, 6H), 0.14 (s, 3H), 0.16 (s, 3H), 0.90 (s, 9H), 0.99 (s, 9H), 2.41 (s, 3H), 2.73-2.77 (m, 3H), 2.82 (dd, 1H, $J = 13.0, 6.5$ Hz), 3.58-3.61 (m, 2H), 3.66 (dd, 1H, $J = 9.5, 3.5$ Hz), 3.97 (br s, 2H), 5.47 (br s, 1H), 6.77 (d, 1H, $J = 8.5$ Hz), 7.05 (dd, 1H, $J = 8.0, 2.0$ Hz), 7.36 (d, 1H, $J = 2.5$ Hz), 7.38 (d, 2H, $J = 8.0$ Hz), 7.63 (br s, 1H), 8.01 (d, 2H, $J = 8.5$ Hz). HR-FABMS calcd for $\text{C}_{38}\text{H}_{33}\text{BrN}_3\text{O}_3\text{SSi}_2$ ($M+\text{H}^+$); 798.2428, found 798.2418. This compound gradually decomposed during ^{13}C NMR measurement due to its unstability.

**5-(Toluene-4-sulfonyl)-3,5,7,8,9,10-hexahydro-2H-1,5,7-triaza-
acephenanthrylen-6-one-8-(tert-butyldimethylsilyloxymethyl)-10-spiro-4'-(2'-
bromo)-cyclohexa-2',5'-dien-1'-one (21a, 21'a).**

To a stirred solution of **20e** (43.4 mg, 0.0543 mmol) in CF₃CH₂OH (1.5 mL) was added MK10 (31.9 mg) and PIFA (93.4 mg, 0.217 mmol) sequentially at room temperature. The mixture was stirred for 7 h. under the same conditions and then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt/Et₃N= 100:50:0.1) to afford two diastereomers **21a** (13.7 mg, 37.2%) and **21'a** (2.9 mg, 7.8%) respectively as a red amorphous. The ratio of **21a** and **21'a** was determined by HPLC (CHIRALPAK AD-H, flow rate 1.0 mL/min, *n*-hexane/*i*-PrOH=95/5, 25°C).

**7-[2-(3-Bromo-4-hydroxyphenyl)-1-(triisopropylsilyloxymethyl)ethylamino]-1-(
toluene-4-sulfonyl)-3,4-dihydro-1H-pyrrolo[4,3,2-*de*]quinolin-8-one (20b).**

To a stirred solution of monobrominated *N*-tritylated (*L*)-tyrosinol (1.5 g, 3.08 mmol) in CH₂Cl₂ (60 mL) was added DBU (1.98 mL, 9.24 mmol) and triisopropylsilyl chloride (TIPSCl) (2.31 mL, 15.4 mmol) sequentially at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 0.75 h at 0°C. The mixture was then quenched with aqueous saturated NaHCO₃ and extracted with CH₂Cl₂. The combined organics were washed with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=20/1) to give [2-[3-bromo-4-(triisopropylsilyloxy)-phenyl]-1-(triisopropylsilyloxymethyl)ethyl]tritylamine (2.47 g, quant) as a colorless oil.

IR (KBr): ν 3057, 3030, 2943, 2866, 1599, 1493, 1462 cm⁻¹. ¹H NMR (300 MHz): δ 0.96 (s, 18H), 1.06 (s, 6H), 1.09 (s, 12H), 0.91-1.09 (m, 3H), 1.19-1.32 (m, 3H), 2.33-2.39 (m, 2H), 2.66 (m, 1H), 3.05 (dd, 1H, *J* = 9.5, 5.5 Hz), 3.20 (dd, 1H, *J* = 9.5, 4.5 Hz), 6.67 (d, 1H, *J* = 8.5 Hz), 6.71 (dd, 1H, *J* = 8.0, 1.5 Hz), 7.12-7.26 (m, 10H), 7.54 (d, 6H, *J* = 7.5 Hz). ¹³C NMR (75 MHz): δ 11.9, 12.9, 18.0, 18.1, 36.7, 55.6, 64.3, 71.0, 114.6, 119.1, 126.3, 127.8, 128.8, 129.2, 133.2, 134.3, 147.1, 150.9. HR-FABMS calcd for C₄₆H₆₇BrNO₂Si₂ (M+H⁺); 800.3894, found 800.3898.

To a stirred solution of [2-[3-bromo-4-(triisopropylsilyloxy)phenyl]-1-(triisopropyl-

silyloxymethyl)ethyl]tritylamine (2.53 g, 3.16 mmol) in THF (125 mL) was added TBAF (3.16 mL (1.0 M solution in THF), 3.16 mmol) at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 0.5 h at 0°C. The mixture was then quenched with aqueous saturated NH₄Cl and extracted with AcOEt. The combined organics were washed with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=10/1) to give [2-[3-bromo-4-hydroxyphenyl]-1-(triisopropylsilyloxymethyl)ethyl]tritylamine (1.83 g, 90%) as a colorless oil.

IR (KBr): ν 2941, 2864, 1493, 1462, 1448 cm⁻¹. ¹H NMR (300 MHz): δ 0.97 (s, 18H), 0.93-1.01 (m, 3H), 2.32-2.45 (m, 2H), 2.70 (m, 1H), 3.02 (dd, 1H, *J* = 9.5, 5.5 Hz), 3.18 (dd, 1H, *J* = 9.5, 4.0 Hz), 5.38 (br s, 2H), 6.80 (s, 2H), 7.09 (s, 1H), 7.13-7.26 (m, 9H), 7.54 (d, 6H, *J* = 7.5 Hz). ¹³C NMR (75 MHz): δ 11.9, 17.7, 36.6, 55.4, 64.1, 71.0, 109.7, 115.4, 126.3, 127.8, 128.7, 130.3, 132.9, 133.0, 147.1, 150.3. HR-FABMS calcd for C₃₇H₄₇BrNO₂Si (M+H⁺); 644.2559, found 644.2583.

0.1N MeOH solution of HCl (1.0 mL) was added to [2-[3-bromo-4-hydroxyphenyl]-1-(triisopropylsilyloxymethyl)ethyl]tritylamine (37.1 mg, 0.0575 mmol) at room temperature under a nitrogen atmosphere and the mixture was stirred for 30 min. The above mixture was added dropwise to a stirred solution of **16b** (20.5 mg, 0.0575mmol) in MeOH (1.0 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred for 24 h under the same conditions and was then concentrated *in vacuo*. The residue was purified by flash chromatography (CH₂Cl₂/MeOH/Et₃N=100:5:0.1) to give **20b** (23.0 mg, 55%) as a red amorphous solid.

IR (KBr): ν 2941, 2864, 1666, 1612, 1556, 1537 cm⁻¹. ¹H NMR (500 MHz, CD₃OD): δ 1.01-1.11 (m, 21H), 2.42 (s, 3H), 2.79 (t, 2H, *J* = 8.0 Hz), 2.76-2.89 (m, 2H), 3.59-3.63 (m, 1H), 3.78 (dd, 1H, *J* = 10.0, 4.0 Hz), 3.97 (t, 2H, *J* = 7.5 Hz), 5.51 (br s, 1H), 6.77 (d, 1H, *J* = 7.5 Hz), 7.02 (dd, 1H, *J* = 8.0, 2.0 Hz), 7.31 (d, 1H, *J* = 2.0 Hz), 7.39 (d, 1H, *J* = 8.0 Hz), 7.68 (br s, 1H), 8.01 (d, 2H, *J* = 8.5 Hz). ¹³C NMR (75 MHz, CD₃OD): δ 9.19, 9.30, 13.0, 18.4, 21.8, 36.2, 43.6, 47.1, 59.3, 64.9, 86.9, 110.7,

117.4, 120.0, 124.0, 129.1, 130.1, 130.4, 130.7, 130.9, 131.2, 134.5, 135.0, 148.6, 154.3, 157.8, 166.9. HR-FABMS calcd for $C_{33}H_{43}BrN_3O_3SSi$ ($M+H^+$); 726.2033, found 726.2029.

5-(Toluene-4-sulfonyl)-3,5,7,8,9,10-hexahydro-2H-1,5,7-triaza-acephenanthrylen-6-one-8-(triisopropylsilyloxymethyl)-10-spiro-4'-(2'-bromo)-cyclohexa-2',5'-dien-1'-one (21b, 21'b).

To a stirred solution of **20b** (9.2 mg, 0.013 mmol) in CF_3CH_2OH (0.8 mL) was added MK10 (4.0 mg) and PIFA (6.7 mg, 0.016 mmol) sequentially at room temperature. The mixture was stirred for 45 min under the same conditions and then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt/ Et_3N =100:50:0.1) to afford two diastereomers **21b** (2.0 mg, 22%) and **21'b** (1.5 mg, 15%) respectively as a red amorphous solid.

21b (less polar): IR (KBr): ν 2943, 2864, 1659, 1574, 1528, 1479, 1462 cm^{-1} . 1H NMR (500 MHz): δ 1.04-1.25 (s, 21H), 1.59 (d, 1H, J = 17.0 Hz), 1.73 (t, 1H, J = 11.5 Hz), 2.40 (s, 3H), 2.60 (t, 2H, J = 7.0 Hz), 3.55-3.61 (m, 2H), 3.80-3.86 (m, 2H), 4.07 (dt, 1H, J = 17.5, 7.5 Hz), 6.15 (br s, 1H), 6.27 (d, 1H, J = 10.0 Hz), 6.97 (dd, 1H, J = 9.5, 3.5 Hz), 7.27 (d, 1H, J = 2.5 Hz), 7.29 (d, 1H, J = 8.5 Hz), 7.43 (s, 1H), 8.02 (d, 2H, J = 8.0 Hz). ^{13}C NMR (125 MHz): δ 11.9, 17.5, 18.0, 21.7, 36.7, 43.9, 49.7, 66.6, 104.1, 118.5, 122.0, 125.4, 125.9, 126.0, 128.8, 129.7, 134.7, 142.0, 145.7, 152.8, 152.7, 157.1, 168.4, 179.0. UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 487 (2300), 329 (12400), 235 nm (30200). HR-FABMS calcd for $C_{33}H_{43}BrN_3O_3SSi$ ($M+H^+$); 724.1876, found 724.1888.

21'b (polar): IR (KBr): ν 2943, 2864, 1661, 1574, 1528, 1479, 1462 cm^{-1} . 1H NMR (500 MHz): δ 1.01-1.17 (s, 21H), 1.59 (d, 1H, J = 13.0 Hz), 1.73 (t, 1H, J = 11.5 Hz), 2.40 (s, 3H), 2.54-2.64 (m, 2H), 3.56-3.61 (m, 2H), 3.76-3.84 (m, 2H), 4.04 (dt, 1H, J = 18.0, 7.0 Hz), 6.18 (br s, 1H), 6.31 (d, 1H, J = 9.5 Hz), 6.89 (dd, 1H, J = 10.0, 2.5 Hz), 7.29 (d, 1H, J = 8.5 Hz), 7.41 (d, 1H, J = 2.5 Hz), 7.43 (s, 1H), 8.02 (d, 2H, J = 8.5 Hz). ^{13}C NMR (125 MHz): δ 11.9, 17.6, 18.0, 21.7, 36.9, 44.1, 49.5, 49.7, 66.5, 104.1, 118.5, 121.9, 123.9, 125.0, 125.5, 126.0, 128.8, 129.7, 134.7, 142.1, 145.7, 152.3, 152.9, 157.1,

168.4, 179.0. UV/Vis (CHCl₃): λ_{max} (ϵ) = 484 (2300), 331 (13000), 232 nm (29000). HR-FABMS calcd for C₃₃H₄₃BrN₃O₃SSi ($M+H^+$); 724.1876, found 724.1887.

7-[2-(3-Bromo-4-hydroxyphenyl)-1-(*tert*-butyldiphenylsilyloxymethyl)ethylamino]-1-(toluene-4-sulfonyl)-3,4-dihydro-1*H*-pyrrolo[4,3,2-*de*]quinolin-8-one (20c).

To a stirred solution of monobrominated *N*-tritylated (*L*)-tyrosinol (177.1 mg, 0.363 mmol) in CH₂Cl₂ (2.5 mL) was added DBU (0.27 mL, 1.82 mmol) and *tert*-butyldiphenylsilyl chloride (TBDPSCI) (0.28 mL, 1.09 mmol) sequentially at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 2 h at 0°C. The mixture was then quenched with aqueous saturated NaHCO₃ and extracted with CH₂Cl₂. The combined organics were washed with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=30/1) to give [2-[3-bromo-4-(*tert*-butyldiphenylsilyloxy)phenyl]-1-(*tert*-butyldiphenylsilyloxymethyl)ethyl]tritylamine (160.3 mg, 46%) as a colorless oil.

IR (KBr): ν 3069, 2930, 2856, 1493, 1472, 1448, 1427 cm⁻¹. ¹H NMR (300 MHz): δ 1.10 (s, 9H), 1.19 (s, 9H), 2.21 (dd, 1H, J = 13.0, 4.0 Hz), 2.39 (dd, 1H, J = 13.0, 9.0 Hz), 2.70 (m, 1H), 3.18 (dd, 1H, J = 9.0, 4.0 Hz), 3.29 (dd, 1H, J = 10.0, 3.5 Hz), 6.28 (d, 1H, J = 8.5 Hz), 6.34 (d, 1H, J = 8.5 Hz), 7.18-7.77 (m, 36H). ¹³C NMR (75 MHz): δ 19.3, 19.7, 26.5, 27.0, 36.9, 55.4, 64.4, 71.1, 114.1, 119.1, 126.2, 127.6, 127.7, 127.8, 128.7, 128.8, 129.5, 129.6, 130.0, 132.4, 133.3, 133.6, 134.1, 135.5, 135.6, 135.7, 146.9, 150.3. HR-FABMS calcd for C₆₀H₆₇BrNO₂Si₂Na ($M+Na^+$); 986.3400, found 986.3399.

To a stirred solution of [2-[3-bromo-4-(*tert*-butyldiphenylsilyloxy)phenyl]-1-(*tert*-butyldiphenylsilyloxymethyl)ethyl]tritylamine (79.8 mg, 0.083 mmol) in THF (1.0 mL) was added TBAF (0.08 mL (1.0 M solution in THF), 0.08 mmol) at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 0.5 h at 0°C. The mixture was then quenched with aqueous saturated NH₄Cl and extracted with AcOEt. The combined organics were washed with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt=10/1) to give [2-[3-bromo-4-

hydroxyphenyl]-1-(*tert*-butyldiphenylsilyloxymethyl)ethyl]tritylamine (47.1 mg, 78%) as a colorless oil.

IR (KBr): ν 2930, 2862, 1493, 1470, 1448, 1427 cm^{-1} . ^1H NMR (300 MHz): δ 1.09 (s, 9H), 2.28 (dd, 1H, J = 13.0, 4.0 Hz), 2.40 (dd, 1H, J = 13.0, 9.0 Hz), 2.73 (m, 1H), 3.16 (dd, 1H, J = 10.0, 5.0 Hz), 3.30 (dd, 1H, J = 10.0, 3.5 Hz), 5.34 (br s, 1H), 6.68 (dd, 1H, J = 8.0, 2.0 Hz), 6.77 (d, 1H, J = 8.5 Hz), 7.04 (d, 1H, J = 1.5 Hz), 7.15-7.45 (m, 15H), 7.52 (d, 6H, J = 7.0 Hz), 7.60 (d, 2H, J = 6.5 Hz), 7.67 (d, 2H, J = 6.5 Hz). ^{13}C NMR (75 MHz): δ 19.3, 27.0, 36.8, 55.4, 64.4, 71.1, 109.7, 115.4, 126.3, 127.6, 127.8, 128.7, 129.6, 129.6, 130.2, 132.7, 133.1, 133.5, 133.6, 135.0, 135.7, 146.9, 150.2. HR-FABMS calcd for $\text{C}_{44}\text{H}_{44}\text{BrNO}_2\text{SiNa}$ ($\text{M}+\text{Na}^+$); 748.2223, found 748.2206.

0.1N MeOH solution of HCl (3.0 mL) was added to [2-[3-bromo-4-hydroxyphenyl]-1-(*tert*-butyldiphenylsilyloxymethyl)ethyl]tritylamine (146.0 mg, 0.201 mmol) at room temperature under a nitrogen atmosphere and the mixture was stirred for 30 min. The above mixture was added dropwise to a stirred solution of **16b** (71.6 mg, 0.201 mmol) in MeOH (3.0 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred for 24 h under the same conditions and was then concentrated *in vacuo*. The residue was purified by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{Et}_3\text{N}$ =100:5:0.1) to give **20c** (97.4 mg, 60%) as a red amorphous solid.

20c: IR (KBr): ν 2930, 2856, 1666, 1580, 1556, 1537 cm^{-1} . ^1H NMR (500 MHz, CD_3OD): δ 1.04 (s, 9H), 2.36 (s, 3H), 2.78 (t, 2H, J = 7.5 Hz), 2.83 (dd, 1H, J = 13.5, 6.5 Hz), 2.90 (dd, 1H, J = 13.5, 7.5 Hz), 3.50-3.52 (m, 2H), 3.66-3.68 (m, 1H), 3.94 (t, 2H, J = 7.5 Hz), 5.28 (br s, 1H), 6.78 (d, 1H, J = 8.5 Hz), 6.98-7.02 (m, 3H), 7.20 (t, 1H, J = 7.5 Hz), 7.27 (t, 1H, J = 7.5 Hz), 7.33-7.38 (m, 6H), 7.50 (d, 2H, J = 6.5 Hz), 7.70 (br s, 1H), 8.08 (d, 2H, J = 8.0 Hz). ^{13}C NMR (125 MHz, CD_3OD): δ 18.9, 19.9, 21.8, 27.4, 36.0, 43.6, 59.0, 64.0, 87.1, 110.8, 117.4, 119.9, 124.2, 128.8, 128.9, 130.3, 130.6, 130.7, 130.9, 131.0, 131.3, 133.8, 133.9, 134.6, 134.9, 136.6, 136.7, 148.7, 153.3, 154.3, 157.8, 166.8. HR-FABMS calcd for $\text{C}_{42}\text{H}_{43}\text{BrN}_3\text{O}_5\text{SSi}$ ($\text{M}+\text{H}^+$); 808.1876, found 808.1848.

**5-(Toluene-4-sulfonyl)-3,5,7,8,9,10-hexahydro-2H-1,5,7-triaza-
acephenanthrylen-6-one-8-(tert-butyldiphenylsilyloxymethyl)-10-spiro-4'-(2'-
bromo)-cyclohexa-2',5'-dien-1'-one (21c, 21'c).**

To a stirred solution of **20c** (33.8 mg, 0.0418 mmol) in CF₃CH₂OH (1.5 mL) was added MK10 (7.3 mg) and PIFA (21.6 mg, 0.0501 mmol) sequentially at room temperature. The mixture was stirred for 45 min. under the same conditions and then concentrated *in vacuo*. The residue was purified by flash chromatography (n-hexane/AcOEt/Et₃N= 100:50:0.1) to afford two diastereomers **21c** (6.4 mg, 19%) and **21'c** (4.3 mg, 13%) respectively as a red amorphous solid.

21c (less polar): IR (KBr): ν 1661, 1528, 1483, 1460, 1379 cm⁻¹. ¹H NMR (500 MHz): δ 1.08 (s, 9H), 1.51 (d, 1H, *J* = 13.0 Hz), 1.68 (t, 1H, *J* = 11.5 Hz), 2.41 (s, 3H), 2.60 (t, 2H, *J* = 7.5 Hz), 3.55 (m, 2H), 3.71 (dd, 1H, *J* = 10.0, 3.5 Hz), 3.82 (dt, 1H, *J* = 17.5, 8.5 Hz), 4.07 (dt, 1H, *J* = 18.0, 7.0 Hz), 6.12 (br s, 1H), 6.25 (d, 1H, *J* = 10.0 Hz), 6.89 (dd, 1H, *J* = 9.5, 2.5 Hz), 7.22 (d, 1H, *J* = 2.0 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 7.37-7.44 (m, 7H), 7.63 (d, 4H, *J* = 7.5 Hz), 8.04 (d, 2H, *J* = 8.0 Hz). ¹³C NMR (75 MHz): δ 17.5, 19.2, 21.7, 26.9, 36.5, 43.8, 49.4, 49.7, 66.7, 104.1, 118.5, 121.8, 121.9, 125.4, 125.8, 126.1, 127.9, 128.7, 129.7, 130.0, 132.6, 132.7, 134.6, 135.5, 141.9, 145.7, 152.2, 152.7, 157.1, 168.4, 179.0. UV/Vis (CHCl₃): λ_{max} (ϵ) = 485 (1900), 330 (11100), 230 nm (33100). HR-FABMS calcd for C₄₂H₄₃BrN₃O₅SSi (*M*+H⁺); 806.1720, found 806.1780.

21'c (polar): IR (KBr): ν 1661, 1526, 1487, 1462, 1379 cm⁻¹. ¹H NMR (500 MHz): δ 1.11 (s, 9H), 1.50 (d, 1H, *J* = 14.0 Hz), 1.69 (t, 1H, *J* = 11.5 Hz), 2.43 (s, 3H), 2.61 (t, 2H, *J* = 7.0 Hz), 3.53-3.59 (m, 2H), 3.71-3.86 (m, 2H), 4.06 (dt, 1H, *J* = 18.0, 6.5 Hz), 6.19 (br s, 1H), 6.31 (d, 1H, *J* = 9.5 Hz), 6.86 (dd, 1H, *J* = 9.5, 2.5 Hz), 7.33 (d, 2H, *J* = 7.5 Hz), 7.39-7.47(m, 8H), 7.66 (d, 4H, *J* = 7.0 Hz), 8.06 (d, 2H, *J* = 8.5 Hz). ¹³C NMR (75 MHz): δ 17.6, 19.2, 21.8, 26.9, 36.7, 44.0, 49.4, 49.5, 66.7, 104.1, 118.5, 121.9, 123.8, 124.9, 125.5, 126.0, 127.9, 128.8, 129.7, 130.0, 130.1, 132.6, 132.7, 134.6, 135.5, 135.6, 142.0, 145.8, 152.2, 152.8, 157.0, 168.3, 179.0. UV/Vis (CHCl₃): λ_{max} (ϵ) = 483

(2100), 330 (12400), 230 nm (34600). HR-FABMS calcd for $C_{42}H_{43}BrN_3O_5SSi$ ($M+H^+$); 806.1719, found 806.1711.

5-(Toluene-4-sulfonyl)-3,5,7,8,9,10-hexahydro-2H-1,5,7-triaza-acephenanthrylen-6-one-8-(tert-butyldimethylsilyloxymethyl)-10-spiro-4'-(2'-bromo)-cyclohexa-2',5'-dien-1'-one (21a, 21'a).

To a stirred solution of **20a** (54.1 mg, 0.079 mmol) in anhydrous CH_2Cl_2 (1.6 mL) was added 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (0.21 mL, 1.19 mmol) at room temperature under a nitrogen atmosphere. The mixture was stirred for 7 h under the same conditions and then concentrated *in vacuo* to give **20d**. To a stirred solution of the residue (crude **20d**) in CF_3CH_2OH (1.3 mL) was added MK10 (16.6 mg) and PIFA (67.9 mg, 0.158 mmol) sequentially at room temperature. The mixture was stirred for 1 h under the same conditions and then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt/ Et_3N = 100:50:0.1) to afford two diastereomers **21a** (5.2 mg, 12.8%) and **21'a** (2.9 mg, 7.1%) respectively as a red amorphous solid respectively.

7-[2-(3-Bromo-4-triisopropylsilyloxyphenyl)-1-(tert-butyldimethylsilyloxymethyl)ethylamino]-1-(toluene-4-sulfonyl)-3,4-dihydro-1H-pyrrolo[4,3,2-de]-quinolin-8-one (20f).

To a stirred solution of **20a** (41.3 mg, 0.0603 mmol) in DMF (2.0 mL) was added imidazole (6.2 mL, 0.0905 mmol) and TIPSCl (0.064 mL, 0.302 mmol) sequentially at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 3 h at 0°C. The mixture was then quenched with aqueous saturated $NaHCO_3$ and extracted with AcOEt. The combined organics were washed with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt/ Et_3N =100/100/0.1) to give **20f** (33.0 mg, 65%) as a red oil.

20f: IR (KBr): ν 2947, 2928, 2866, 1661, 1580, 1531, 1493 cm^{-1} . 1H NMR (500 MHz, CD_3OD): δ 0.02 (s, 6H), 0.89 (s, 9H), 1.00-1.32 (m, 21H), 2.42 (s, 3H), 2.73-2.77 (m, 3H), 2.83 (dd, 1H, J = 14.0, 6.5 Hz), 3.54-3.68 (m, 3H), 3.96 (t, 2H, J = 6.5 Hz), 5.48 (br s, 1H), 6.78 (d, 1H, J = 8.5 Hz), 7.04 (dd, 1H, J = 8.0, 2.0 Hz), 7.37 (d, 1H, J = 2.0

Hz), 7.39 (d, 2H, $J = 8.5$ Hz), 7.65 (br s, 1H), 8.02 (d, 2H, $J = 8.5$ Hz). HR-FABMS calcd for $C_{41}H_{59}BrN_3O_5SSi_2$ ($M+H^+$); 840.2897, found 840.2904. This compound gradually decomposed during ^{13}C NMR measurement due to its unstability.

5-(Toluene-4-sulfonyl)-3,5,7,8,9,10-hexahydro-2H-1,5,7-triaza-acephenanthrylen-6-one-8-(tert-butyldimethylsilyloxymethyl)-10-spiro-4'-(2'-bromo)-cyclohexa-2',5'-dien-1'-one (21a, 21'a).

To a stirred solution of **20f** (18.0 mg, 0.0213 mmol) in CF_3CH_2OH (0.7 mL) was added MK10 (12.4 mg) and PIFA (36.6 mg, 0.0852 mmol) sequentially at room temperature. The mixture was stirred for 7 h. under the same conditions and then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt/ Et_3N = 100:50:0.1) to afford two diastereomers **21a** (4.2 mg, 28.8%) and **21'a** (1.1 mg, 7.2%) respectively as a red amorphous solid.

7-[2-(3-Bromo-4-tert-butyldiphenylsilyloxyphenyl)-1-(tert-butyldimethylsilyloxymethyl)ethylamino]-1-(toluene-4-sulfonyl)-3,4-dihydro-1H-pyrrolo[4,3,2-de]-quinolin-8-one (20g).

To a stirred solution of **20a** (43.3 mg, 0.0632 mmol) in THF (2.0 mL) was added imidazole (12.9 mg, 0.190 mmol) and TBDPSCl (0.049 mL, 0.190 mmol) sequentially at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 4 h at 0°C. The mixture was then quenched with aqueous saturated $NaHCO_3$ and extracted with AcOEt. The combined organics were washed with brine, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt/ Et_3N =100/100/0.1) to give **20g** (22.5 mg, 39%) as a red oil.

20g: IR (KBr): ν 2947, 2928, 2866, 1661, 1580, 1531, 1493 cm^{-1} . 1H NMR (500 MHz, CD_3OD): δ -0.02 (s, 6H), 0.87 (s, 9H), 1.08 (s, 9H), 2.37 (s, 3H), 2.70-2.79 (m, 4H), 3.50-3.52 (m, 2H), 3.61 (dd, 1H, $J = 11.5, 5.5$ Hz), 3.97 (t, 2H, $J = 7.5$ Hz), 5.46 (br s, 1H), 6.34 (d, 1H, $J = 8.0$ Hz), 6.71 (dd, 1H, $J = 8.0, 2.0$ Hz), 7.32-7.36 (m, 5H), 7.39 (d, 4H, $J = 7.0$ Hz), 7.68 (br s, 1H), 7.68 (d, 4H, $J = 7.0$ Hz), 7.99 (d, 2H, $J = 8.0$ Hz). HR-FABMS calcd for $C_{48}H_{57}BrN_3O_5SSi_2$ ($M+H^+$); 922.2741, found 922.2740. This

compound gradually decomposed during ^{13}C NMR measurement due to its unstability.

**5-(Toluene-4-sulfonyl)-3,5,7,8,9,10-hexahydro-2H-1,5,7-triaza-
acephenanthrylen-6-one-8-(tert-butyldimethylsilyloxymethyl)-10-spiro-4'-(2'-
bromo)-cyclohexa-2',5'-dien-1'-one (21a, 21'a).**

To a stirred solution of **20g** (7.8 mg, 0.0084 mmol) in $\text{CF}_3\text{CH}_2\text{OH}$ (0.5 mL) was added MK10 (6.2 mg) and PIFA (18.2 mg, 0.0422 mmol) sequentially at room temperature. The mixture was stirred for 24 h. under the same conditions and then concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane/AcOEt/ Et_3N = 100:50:0.1) to afford two diastereomers **21a** (2.1 mg, 37.0%) and **21'a** (0.7 mg, 12.0%) respectively as a red amorphous solid.

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F:\TSDISCORHARDIN-MODEL\DISMO

DFILE COMET
 DATIM Fri Jan 29 11:27:06 1999
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 10000.0 Hz
 SCANS 48
 ACQTM 3.277 sec
 PD 3.723 sec
 PW1 5.3 us
 IRNUC 1H
 CTEMP 27.7 C
 SLVNT CDCL3
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 16

DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRO
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

F:\TSDISCORHARDIN-MODEL\DISMO
 Fri Jan 29 12:56:56 1999
 13C
 BCM

75.45 MHz
 124.00 KHz
 1840.0 Hz
 32768
 20408.1 Hz
 1016
 1.606 sec
 1.394 sec
 4.0 us
 1H
 26.7 C
 CDCL3
 77.00 ppm
 0.12 Hz
 24

DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRO
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

F:\MODEL-SAC\252.ALS

Fri Jul 13 13:50:25 2001

1H
NON

300.40 MHz
 130.00 KHz
 1150.0 Hz
 32768

6013.2 Hz

32

5.449 sec

1.551 sec

5.8 us

1H

20.7 C

CDCL3

7.26 ppm

1.20 Hz

15

DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRO
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

F:\MODEL-SAC\252-C.ALS
 Fri Jul 13 14:22:50 2001
 13C
 BCM

75.45 MHz
 124.00 KHz
 1840.0 Hz
 32768
 20408.1 Hz
 522
 1.606 sec
 1.394 sec
 5.0 us
 1H
 20.9 C
 CDCL3
 77.00 ppm
 1.20 Hz
 25

9a

DFILH
COMNT
DATIN
OBNUC
EXMOI
OBFRG
OBSEI
OBFIH
POINT
FREQU
SCANS
ACQTN
PD
PWL
IRNUC
CTEMI
SIVNT
EXREI
BF
RGAIN

D:\DISCOMODEL\P-MEONSTAIL13

DFILE COMNT
DATIM Sun Apr 27 20:48:22 2003
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 3911
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.3 us
IRNUC 1H
CTEMP 23.5 c
SIVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24

F:\TSDISORHABDIN-MODEL\DIS

Thu Feb 25 21:28:28 1999

1H
NON

300.40 MHz
130.00 KHz
1150.0 Hz
32768
10000.0 Hz

48
3.277 sec
3.723 sec
5.3 us

20.1 C

CDCL3

7.26 ppm
0.12 Hz
21

FILE
COMNT
DATIM
OENUC
EXMOD
OBFRO
OBFRO
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

F:\TSDISCORHABDIN-MODEL\DISM

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFREQ
OBFSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Fri Feb 26 14:01:26 1999
13C
BCM

67.80 MHz
135.00 KHz
5200.0 Hz
32768
18315.0 Hz
2328
1.789 sec
1.211 sec
4.0 us
1H
18.3 c
CDCL3
77.00 ppm
0.12 Hz
26

1H Line

Date : Tue Feb 18 15:55:26 2003
 FileName : gouseiyndismode18sc009
 Comment : 1H Line
 SliceHistory :
 EXMODE : bcm

POINT : 16384 points
 SAMPD : 16384 points
 FREQ : 300300.0 Hz
 FILTR : 15000 Hz
 DELAY : 13.3 usec
 DEADT : 16.0 usec
 INTEL : 33.3 usec
 TIMES : 1000000 times
 DUMMY : 1 times
 PD : 2.4544 sec
 ACQTM : 545.5872 msec
 PREOL : 0.01000 msec
 INIIT : 1000.0000 msec
 RESOL : 1.83 Hz
 PW1 : 8.00 usec
 13C : 125.65 MHz
 OBSFQ : 127958.00 Hz
 RGAIN : 29
 1H : 500.00 MHz
 OBSFQ : 162160.00 Hz
 IRFQ : 65.0 usec
 IRPFW : 0
 IRPWS : 0

SCANS : 6413 times
 SLVNT : CDCL3
 SPINNT : 13 Hz
 TEMP : 29.2 C

F:\TSD\DISCORHABDIN-MODEL\DISMODEL-

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFREQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Fri Feb 19 20:46:08 1999
1H
NON

300.40 MHz
130.00 KHz
1150.0 Hz
32768
10000.0 Hz
48
3.277 sec
3.723 sec
5.3 us
1H
19.7 c
CDCL3
7.24 ppm
1.20 Hz
22

12

S45

F:\TSD\DISCORHABDIN-MODEL\DISMODEL

DFILE COMNT
 DATIM Wed Feb 10 17:00:01 1999
 OBNUC 13C
 EXMOD BCM
 OBFRQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.0 Hz
 POINT 32768
 FREQU 18315.0 Hz
 SCANS 1036
 ACQTM 1.789 sec
 PD 1.211 sec
 PW1 4.0 us
 IRNUC 1H
 CTMP 16.9 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 26

DFILE COMNT DATM OBNUC EXMOD OBFRQ OBSET OBFIN POINT FREQU SCANS ACQTM PD PW1 IRNUC CTEMP SLVNT EXREF BF RGAIN

F:\1500-1700\EGI941522.ALS
 Thu Dec 03 21:33:29 1998
 1H
 NON
 300.40 MHz
 130.00 KHz
 1150.0 Hz
 32768
 10000.0 Hz
 48
 3.277 sec
 3.723 sec
 5.3 us
 1H
 CDCL3
 24.5 C
 7.26 ppm
 0.12 Hz
 24

C:\WINNMR95\COMMON_DEFAULT
 COMNT model-skannka-dmsc
 DATIM Fri Jul 27 09:01:19 2001
 OBNUC 1H
 EXMOD DIFNOE
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 1484
 ACQTM 5.449 sec
 PD 5.000 sec
 PW1 11.5 us
 IRNUC 1H
 CTEMP 20.7 c
 SLVNT DMSO
 EXREF 2.49 ppm
 BF 0.12 Hz
 RGAIN 18

HB

HA

HC

HD

F:\13C\MODEL-SKANKA\AUTO1BCM

DFILE COMNT
COMNT
DATIM
OBNUC
EXMOD
OBFRO
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Fri Jul 27 13:00:21 2001

13C
BCM

75.45 MHz
124.00 KHz
1840.0 Hz
32768
20408.1 Hz
1600
1.606 sec
1.394 sec
4.0 us
1H
21.5 C
DMSO
39.50 ppm
1.20 Hz
23

DFILE F:\4\020012.ALS
 COMNT Sat Apr 27 15:27:26 2002
 DATIM 1H
 OBNUC NON
 EXMOD
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 24.8 C
 SLVNT CDCL3
 EXREF 3.06 ppm
 BF 1.20 Hz
 RGAIN 24

DFILE F:\399-C.ALS
 COMNT Sat Jul 07 19:13:21 2001
 DATIM
 OBNUC 13C
 EXMOD BCM
 OBFRO 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 712
 ACQTM 1.606 sec
 PD 1.394 sec
 PW1 5.0 us
 IRNUC 1H
 CTEMP 21.5 C
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 23

F:\408.ALS

Mon Jul 09 12:10:25 2001

DFILE
COMMT
DATIM
OBNUC
EXMOD
OBFRO
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

1H
NON

300.40 MHz
130.00 KHz
1150.0 Hz
32768
6013.2 Hz
32
5.449 sec
1.551 sec
5.8 us
1H
21.3 C
CDCL3
7.58 ppm
0.12 Hz
13

DFILE F:\408-C.ALS
 COMNT Mon Jul 09 12:38:06 2001
 DATIM 13C
 OBNUC BCM
 EXMOD
 OBFRQ 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 536
 ACQTM 1.606 sec
 PD 1.394 sec
 PW1 5.0 us
 IRNUC 1H
 CTEMP 21.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 25

19a

F:\411-C.ALS
Mon Jul 09 13:30:19 2001
13C
BCM

-5.433
-5.458

18.114

25.877

37.605

55.127

62.280

71.074

76.580

77.000

77.429

77.429

569.60

15,480

226.277

27.834

7.69-8.72

30.315

32.878

33.373

666

47.120

608.05

75.45 MHz	21.5 °C
124.00 KHz	
1840.0 Hz	
32768	
20408.1 Hz	
872	
1.606 sec	
1.394 sec	
5.0 us	
1H	
CDCL3	
77.00 ppm	
0.12 Hz	
23

1H Line

Date : Mon Apr 14 14:36:12 2003
 File Name : LoadingFID.mdata
 Comment : 1H Line
 Slice History : non
 EXMODE : non

POINT 16384 points
 SAMP0 16384 points
 FREQ0 10000.0 Hz
 DELAY 5000 Hz
 FILTR 40.0 usec
 DEADT 58.7 usec
 INVL 100.0 usec
 TIMES 64 times
 DUMY 64 times
 PD 5.3616 sec
 ACQTM 1638.3999 msec
 PREDL 0.01000 msec
 INVT 1000.0000 msec
 RESOL 0.61 Hz
 PM1 2.63 usec
 1H 500.00 MHz
 162167.63 Hz
 23
 SCANS 64 times
 SLVNT CD300
 SPINNING 11 Hz
 TEMP 26.6 C

1H Line

Date : Mon Apr 14 15: 43: 28 2003
 FileName : gousei\VTBScourc\mg130
 Comment : 1H Line
 SliceHistory :
 EXMODE : bcn

POINT : 16384 points
 SAMPD : 16384 points
 FREQU : 30030.0 Hz
 DELAY : 15.00 Hz
 DEACT : 13.3 usec
 INTVL : 16.0 usec
 TIMES : 33.3 usec
 DUMMY : 1 times
 PD : 1000000 times
 ACQTM : 2.4544 sec
 PREDL : 545.5872 msec
 INVT : 0.0100 msec
 RESOL : 1000.0000 msec
 PW1 : 1.83 Hz
 13C : 8.00 usec
 OBNUC : 13C
 OBFRQ : 125.65 MHz
 OBSET : 127958.00 Hz
 RGAIN : 29
 IRNUC : 1H
 IRFRQ : 500.00 MHz
 IRSET : 162160.00 Hz
 IRPPI : 85.0 usec
 TRNS : 0

SCANS : 2169 times
 SLVNT : CD300
 SPINNING : 13 Hz
 TEMP : 29.5 C

1H Line

Date : Tue Dec 10 10:38:09 2002

File Name : gauseiyhsu01ue ~ca-3

Comment : 1H Line

SlicesHistory

EXMODE : non

POINT 16384 points
 SAMPD 16384 points
 FREQU 10000.0 Hz
 FILTR 5000 Hz
 DELAY 40.0 usec
 DEADT 58.7 usec
 INTVL 100.0 usec
 TIMES 32 times
 DUMMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3999 msec
 PREDL 0.01000 msec
 INTIM 1000.0000 msec
 RESOL 0.81 Hz
 PUL 2.63 usec
 OBNUC 1H
 OBFRQ 500.00 MHz
 OBSET 162167.63 Hz
 RGAIN 25
 SCANS 32 times
 SLVNT CDCL3
 SPINNING 12 Hz
 TEMP 26.8 C

Date : Mon Jul 1 15:27:00 2002
FileName : LoadingFID.nmdata
Comment : 1H Line
SliceHistory :
EXMODE : noe_dif
POINT : 16384 points
SAMPD : 16384 points
FREGU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 54.5 usec
INVL : 100.0 usec
TIMES : 160 times
DUMMY : 4 times
PD : 10.0000 sec
ACQTM : 1638.3999 msec
PREDL : 0.01000 msec
INITI : 1000.0000 msec
RESOL : 0.61 Hz
PWI : 11.00 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
ORSET : 162167.63 Hz
RGAIN : 15
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 161663.01 Hz
IRST2 : 0.00 Hz
IRATN : 350
SCANS : 160 times
SLVNT : CDCL3
SPINNT : 13 Hz
TEMP : 22.5 C

H^A

4.99

H^B

10.44

1.72

1.53
1.22

Date : Mon Jul 1 13:59:30 2002
FileName : LoadingID.nmdata
Comment : 1H Line
SliceHistory : noe_dif
EXMODE :
POINT : 16384 points
SAMPD : 16384 points
FREQ : 10000.0 Hz
FILT : 5000 Hz
DELTA : 40.0 usec
DEAD : 54.5 usec
INTVL : 100.0 usec
TIMES : 320 times
DUMMY : 4 times
P1 : 10.0000 sec
ACQTM : 1638.3999 msec
PREDL : 0.01000 msec
ININT : 1000.0000 msec
RESOL : 0.61 Hz
PW1 : 11.00 usec
1H : 500.00 MHz
OBNUC : 162167.83 Hz
OBSET : 15
RGAIN : 1H
IRNUC : 500.00 MHz
IRFRQ : 163413.97 Hz
IRST2 : 0.00 Hz
IRATN : 350
SCANS : 320 times
SLVNT : CDCL3
SPINNT : 14 Hz
TEMP : 22.9 C

H_B

5.27

H_A

17.19

1H Line

Date : Mon Dec 9 20:59:27 2002

File Name : gouseiyhsup1ue13C.mn
 Comment : 1H Line
 Slice History :
 EXMODE : bcm

POINT 16384 points
 SAMPD 16384 points
 FREQU 30030.0 Hz
 FILTR 15000 Hz
 DELAY 13.3 usec
 DEADT 16.0 usec
 INTVL 33.3 usec
 TIMES 100000 times
 DUMMY 1 times
 PD 2.4544 sec
 AGTM 545.5872 msec
 PREDL 0.010000 msec
 INIWT 1000.0000 msec
 RESOL 1.83 Hz
 PW1 8.00 usec
 13C 135.65 MHz
 OBFRQ 127958.00 Hz
 RGAIN 28
 1H 500.00 MHz
 IRFRQ 162160.00 Hz
 IRPWA 85.0 usec
 IRPWS 0

SCANS 5310 times
 SLVNT CDCl3
 SPINNING 13 Hz
 TEMP 29.3 C

DFILE F:\SPIRO-SITA.ALS
 COMMT Fri Aug 03 19:11:31 2001
 DATIM 1H
 OBNUC NON
 EXMOD
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 64
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 21.1 C
 SLVNT CDCL3
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 21

1H Line

Date : Tue Nov 12 20:57:15 2002

FileName : LoadingID.nmdata
 Comment : 1H Line
 SliceHistory :
 EXMODE : noe_dif

POINT : 16384 points
 SAMP0 : 16384 points
 FREQU : 10000.0 Hz
 FLTR : 5000 Hz
 DELAY : 40.0 usec
 DEATH : 54.5 usec
 INTVL : 100.0 usec
 TIMES : 600 times
 DUMMY : 4 times
 PD : 10.0000 sec
 ACQTM : 1638.3959 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.51 Hz
 PW1 : 11.00 usec
 1H : 500.00 MHz
 OBNUC : 162167.63 Hz
 OBFRQ : 19
 RGAIN : 1H
 IRNUC : 500.00 MHz
 IRFRQ : 161686.67 Hz
 IRST2 : 0.00 Hz
 IRATN : 350
 SCANS : 600 times
 SLVNT : CDCL3
 SPINNING : 13 Hz
 TEMP : 26.6 C

H_A

3.27

11.44

H_B

0.08

Date : Tue Nov 12 16:57:40 2002

FileName : LoadingFID.nacata
Comment : 1H Line
SliceHistory :
EXMODE : noe_dif

POINT : 16384 points
SAMP0 : 16384 points
FREQ0 : 10000.0 Hz
FILT0 : 5000 Hz
DELAY : 40.0 usec
DEADT : 54.5 usec
INVT0 : 100.0 usec
TIMES : 1000 times
DUMMY : 4 times
PD : 10.0000 sec
ACQTM : 1638.3999 msec
PREDL : 0.01000 msec
INVT0 : 1000.0000 msec
RESOL : 0.61 Hz
PW1 : 11.00 usec
1H : 500.00 MHz
OBNUC : 162167.63 Hz
OBFRQ : 19
OBSET :
RGAIN :
IRNUC : 500.00 MHz
IRFRQ : 163632.47 Hz
IRSET : 0.00 Hz
IRST2 : 350
IRATN :
SCANS : 1000 times
SLVNT : CDCL3
SPINNING : 8 Hz
TEMP : 26.5 C

1H Line

Date : Tue Apr 9 21:00:03 2002
 FileName : gouseiyhsp131313.r35:3
 Comment : 1H Line
 SliceHistory :
 EXMODE : bcm

POINT 16384 points
 SAMPO 16384 points
 FREQ 30030.0 Hz
 FILTR 15000 Hz
 DELAY 13.3 usec
 DEADT 16.0 usec
 INTVL 33.3 usec
 TIMES 1000000 times
 DUMMY 1 times
 PD 2 4544 sec
 ACQTM 545 5872 msec
 PREDI 0 01000 msec
 INMT 1000 0000 msec
 RESOL 1.83 Hz
 PW1 8.00 usec
 OBNUC 13C 125.65 MHz
 OBPRG 127958.00 Hz
 OBSET 11
 RGAIN 11
 IRNUC 1H 500.00 MHz
 IRPRG 162160.00 Hz
 IRSET 65.0 usec
 IRPW 0
 IRRNS 0

SCANS : 13052 times
 SLVNT : CDCL3
 SPINNING : 7 Hz
 TEMP : 27.5 C

F:\OH-UP.ALS

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRO
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Fri Jan 25 20:05:34 2002

1H
NON

300.40 MHz
130.00 KHz
1150.0 Hz
32768
6013.2 Hz
64
5.449 sec
1.551 sec
5.8 us
22.5 C
ACETN
5.61 ppm
1.20 Hz
21

DFILE COMNT
 DATIM Fri Jan 25 09:33:31 2002
 OBNUC 13C
 EXMOD BCM

75.45 MHz
 124.00 KHz
 1840.0 Hz
 32768
 20408.1 Hz
 10914
 1.606 sec
 1.394 sec
 PD
 PW1 5.0 us
 IRNUC 1H
 CTEMP 23.5 C
 SLVNT ACETN
 EXREF 29.80 ppm
 BF 0.12 Hz
 RGAIN 23

C:\WINNMR95\COMMON\DEFAULT.ALS

DFILE 991109-2
 COUNT Thu Nov 21 14:51:39 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 9
 ACQTM 5.449 sec
 PD 1.551 sec
 FWI 5.5 us
 IRNUC 1H
 CTEMP 22.9 C
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 18

1H Line

Date : Tue Jan 14 21: 09: 53 2003
 FileName : LoadingFID.nmdata
 Comment : 1H Line
 SliceHistory :
 EXMODE : bcm

POINT 16384 points
 SAMPD 16384 points
 FREQD 30030.0 Hz
 FIDTA 15000 Hz
 DELAY 12.3 usec
 DCAOT 16.0 usec
 INVL 33.3 usec
 TIMES 1000000 times
 DUMM 1 times
 PD 2.4544 sec
 ACQTM 545.5872 msec
 PREDL 0.01000 msec
 INIIT 1000 0000 msec
 RESOL 1.83 Hz
 PW1 8.00 usec
 PNUC 13C
 OBFRQ 125.65 MHz
 OBSET 127958.00 Hz
 RGAIN 28
 IRNUC 1H
 IRFRO 500.00 MHz
 IPSET 162160.00 Hz
 IPBPM 65.0 usec
 IPBMS 0
 SCANS 5576 times
 SLVNT : CDCL3
 SPINNING 13 Hz
 TEMP 29.6 C

1H Line

Date : Tue Aug 27 10:30:20 2002
 FileName : gouseyHSS10E1 Acosta3
 Comment : 1H Line
 SliceHistory :
 EXMODE : non

POINT 16384 points
 SAMPD 16384 points
 FREQD 10000.0 Hz
 F1F2 5000 Hz
 DELAY 40.0 usec
 DELDT 58.7 usec
 INTEL 100.0 usec
 TIMES 32 times
 DUMPT 1 times
 PD 5.3616 sec
 ACQTW 1638.3999 msec
 PREDL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 0.61 Hz
 PWT 2.63 usec
 OSNUC 1H
 CBFRO 500.00 MHz
 OBSET 162.6763 Hz
 RGAIN 25

SCANS : 32 times
 SLVNT : CDCL3
 SPINNING 13 Hz
 TEMP 22.8 C

D:\DISCO\L-SITAMICHEAL13C.A

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Mon Apr 21 09:31:54 2003
13C
BCM

75.45 MHz
124.00 KHz
1840.0 Hz
32768
20408.1 Hz
13922
1.606 sec
1.394 sec
4.3 us
20.9 c
CDCl3
77.00 ppm
0.12 Hz
24

1H Line

Date : Tue May 7 21:07:57 2002

Filename : gouselyMcMespive.mda:3

Comment : 1H Line

SliceHistory

EXMODE

non

POINT 16384 points
 SAMPO 16384 points
 FREQ 1000.0 Hz
 FIDTR 5000 Hz
 DELAY 40.0 usec
 DEAT 58.7 usec
 INVT 100.0 usec
 TIMES 160 times
 DUMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3999 msec
 PREDL 0.01000 msec
 INVT 1000.0000 msec
 RESOL 0.61 Hz
 PM1 2.63 usec
 GENUC 500.00 MHz
 DEFRQ 162187.63 Hz
 OBSET 2B
 REGAIN
 SCANS 160 times
 SLVNT CDCL3
 SPINNT 14 Hz
 TEMP 22.8 C

13C Line

Date : Tue May 7 16:39:42 2002
 FileName : gousei\NMR\spine:13C-
 Comment : 13C Line
 SliceHistory :
 EXMODE : bcm

POINT 16384 points
 SAMPD 16384 points
 FREQD 30030.0 Hz
 F1FIR 15000 Hz
 DELAY 13.3 usec
 DEADT 16.0 usec
 INVT 33.3 usec
 TIMES 1000000 times
 DUMMY 1 times
 PD 2.4544 sec
 ACQTM 545.5672 msec
 PREOL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 1.63 Hz
 PW1 8.00 usec
 13C 125.65 MHz
 OBFRQ 127958.00 Hz
 RBSET 29
 RGAIN 29
 TRNUC 1H
 TRFQ 500.00 MHz
 TRSET 162160.00 Hz
 TRPW 85.0 usec
 TRNS 0
 SCANS 7376 times
 SLVNT : CDCL3
 SPINNING 14 Hz
 TEMP 27.3 C

1H Line

Date : Wed May 1 17:01:22 2002
 FileName : gouseiyoMasdis:13.m33
 Comment : 1H Line
 SliceHistory :
 EXMODE : non

POINT : 16384 points
 SAMPD : 16384 points
 FREQ : 1000.0 Hz
 F1F2 : 5000 Hz
 DELAY : 40.0 usec
 DEAT : 58.7 usec
 INVL : 100.0 usec
 TIMES : 10000 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PREDL : 0.01000 msec
 INTM : 1000.0000 msec
 RESOL : 0.61 Hz
 PH1 : 2.83 usec
 OBNIC : 1H
 CBPRQ : 500.00 MHz
 OBSET : 162167.63 Hz
 RGAIN : 26

SCANS : 65 times
 SLVNT : CDCL3
 SPINNING : 10 Hz
 TEMP : 23.5 C

13C Line

Date : Wed May 1 19:43:32 2002

FileName : gouselyh0mespsta1a13C
 Comment : 13C Line
 SliceHistory :
 EXMODE : bcm

POINT 16384 points
 SAMPD 16384 points
 FREQ 300330.0 Hz
 FILTR 15000 Hz
 DELAY 13.3 usec
 DEATH 16.0 usec
 INTVL 33.3 usec
 TIMES 1000000 times
 DUMY 1 times
 PD 2.4544 sec
 ACQTM 545.5872 msec
 PREDL 0.01000 msec
 ININT 1000.0000 msec
 RESOL 1.83 Hz
 PW1 8.00 usec
 DBNJC 13C
 DBFRQ 125.85 MHz
 DBSET 127958.00 Hz
 RGAIN 29
 IRNJC 1H
 IRFRQ 500.00 MHz
 IRSET 162160.00 Hz
 IRPWN 85.0 usec
 IRNRS 0
 SCANS 3160 times
 SLVNT CDCL3
 SPINNT 11 Hz
 SPINNING 26.9 C
 TEMP

DFILE F:\381-1.ALS
 COMNT
 DATIM Thu Jun 14 18:28:06 2001
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 64
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 22.1 c
 SLVNT CDCL3
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 26

```

Date : Tue Aug 28 20:11:21 2001
FileName : .LoadingID.mmdata
Comment : 1H Line
SliceHistory : bcm
EXMODE :

POINT : 16384 points
SAMP0 : 16384 points
FREQ0 : 30300.0 Hz
FILTR : 15000 Hz
DELAY : 13.3 usec
DEAD0 : 16.0 usec
BEAT0 : 33.3 usec
INTVL : 20000 times
TIMES : 1
DUMMY : 2.4544 sec
PD0 : 545.5872 msec
ACQTM : 0.01000 msec
PREDL : 1000.0000 msec
INVTM : 1.83 Hz
RESOL : 8.00 usec
pw1 : 13C
DBNUC : 125.65 MHz
ZBFRQ : 127956.00 Hz
DBSET : 29
RGAIN : 1H
RNUC : 500.00 MHz
RFRQ : 162160.00 Hz
RSET : 85.0 usec
RPNW : 0
RRPW : 0
CANS : 11841 times

LVNT : COOL3
PINNING : 12 Hz
EXP : 26.2 C

```

DAICEL CHIRALCEL OD
Hex/iPrOH 65/35
1.0ml/min 20°C

DFILE F:\381-2.ALS
 COMNT
 DATIM Thu Jun 14 18:41:01 2001
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 64
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 21.7 C
 SLVNT CDCL3
 EXREF 6.08 ppm
 BF 0.12 Hz
 RGAIN 27

27

DFILE F:\511-2-C.ALS
 COMNT
 DATIM Sat Sep 01 13:56:41 2001
 OBNUC 13C
 EXMOD BCM
 OBFRQ 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 1560
 ACQTM 1.606 sec
 PD 1.394 sec
 PW1 5.0 us
 IRNUC 1H
 CTEMP 21.4 C
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

F:\381-3.ALS
 Thu Jun 14 18:15:56 2001
 1H
 NON
 300.40 MHz
 130.00 KHz
 1150.0 Hz
 32768
 6013.2 Hz
 64
 5.449 sec
 1.551 sec
 5.8 us
 1H
 CDCL3
 22.7 C
 6.01 ppm
 0.12 Hz
 26

DFILE F:\HARAYAMA.ALS
 COMNT Sat Jan 19 09:43:28 2002
 DATIM 13C
 OBNUC BCM
 EXMOD
 OBFRO 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 16932
 ACQTM 1.606 sec
 PD 1.394 sec
 PW1 5.0 us
 IRNUC 1H
 CTEMP 24.2 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 24

D:\DISCO-HCL.ALS
 Tue Jul 23 22:08:07 2002
 1H
 NON
 300.40 MHz
 130.00 KHz
 1150.0 Hz
 32768
 6013.2 Hz
 128
 5.449 sec
 1.551 sec
 5.8 us
 1H
 20.7 c
 CD3OD
 3.30 ppm
 0.12 Hz
 24

Date : Tue Oct 16 21:00:30 2001

File Name : LoadingID.rmdata
Comment : 1H Line
Slice History :
EXMODE : bcmPOINT : 16384 points
SAMPD : 16384 points
FREQ : 30090.0 Hz
FILT : 15000 Hz
DELT : 13.3 usec
DEACT : 16.0 usec
INVT : 33.3 usec
TIMES : 1000000 times
DUMMY : 1 times
PD : 2 4544 sec
ACQTM : 545 5872 msec
PREDL : 0 01000 msec
INVT : 1000 0000 msec
RESOL : 1.83 Hz
PWI : 8.00 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz
RGAIN : 11
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
TRPW : 85.0 usec
IRFNS : 0SCANS : 10640 times
SLWT : DMSO
SPINNING : 14 Hz
TEMP : 28.4 C

22

16384	00JUL15
16384	00JUL15
10000.0	HZ
5000	HZ
40.0	usec
58.7	usec
100.0	usec
640	times
1	times
5	3615 sec
1638	3999 usec
0.01000	usec
1000	0000 usec
0.61	HZ
2.63	usec
1H	
500.00	WHZ
162167.63	HZ
25	
640	times
CD300	
14	HZ
27.1	C

DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

D:\DISCO\TIPSCOUPRINGHCLISAL
 Mon Apr 28 09:27:52 2003
 13C
 BCM

75.45 MHz
 124.00 KHz
 1840.0 Hz
 32768
 20408.1 Hz
 15008
 1.606 sec
 1.394 sec
 4.3 us
 1H
 23.5 c
 CD3OD
 49.00 ppm
 0.12 Hz
 24

Date : Tue Mar 25 21:02:24 2003
 File Name : LoadingID.mdata
 Comment : In-Line
 SliceHistory : non
 EXMODE : non

POINT 16384 points
 SAMPD 16384 points
 FREQ 10000.0 Hz
 FILTR 5000 Hz
 DELAY 40.0 usec
 DEAT 58.7 usec
 INTVL 100.0 usec
 TIMES 128 times
 DUMMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3999 msec
 PREL 0.01000 msec
 ININT 1000.0000 msec
 RESOL 0.61 Hz
 PM1 2.63 usec
 DBNUC 1H
 DBFRQ 500.00 MHz
 DBSET 162167.63 Hz
 RAIN 25

SCANS 128 times
 SLVNT CD300
 SPINNING 11 Hz
 TEMP 27.1 C

```

: LoadingFID.mdata
: 1H Line
:
: SliceHistory
: EXMODE
: bcm

```

POINT	:	:	16384 points	:
SAMPLE	:	:	16384 points	:
REGU	:	:	30030.0 Hz	:
FILTR	:	:	15000 Hz	:
DELAY	:	:	13.3 usec	:
DEATH	:	:	16.0 usec	:
INVTVL	:	:	33.3 usec	:
TIMES	:	:	100000 times	:
DUMMY	:	:	1 times	:
PD	:	:	2 4544 sec	:
ACQTM	:	:	545.5872 msec	:
PREDL	:	:	0.01000 msec	:
ININTM	:	:	1000.0000 msec	:
RESOL	:	:	1.83 Hz	:
PW1	:	:	8.00 usec	:
DBNJC	:	:	13C	:
DBFRQ	:	:	125.65 MHz	:
DBSET	:	:	127958.00 Hz	:
AGAIN	:	:	29	:
IRNJC	:	:	1H	:
IRFRQ	:	:	500.00 MHz	:
IRSET	:	:	162160.00 Hz	:
IRAPW	:	:	85.0 usec	:
IRRNS	:	:	0	:
SCANS	:	:	5540 times	:
SLVNT	:	:	CD300	:
SPINNING	:	:	17 Hz	:
TEMP	:	:	29.2 C	:

1H Line

Date : Tue Apr 22 20:59:24 2003

FileName : LoadingFID.nmdata
 Comment : 1H Line
 SliceHistory : non

POINT 16384 points
 SAMPD 16384 points
 FREQ 1000.0 Hz
 F1TR 5000 Hz
 DELAY 40.0 usec
 DEAT 58.7 usec
 INVL 100.0 usec
 TIMES 500 times
 DUMMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3999 msec
 PREOL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 0.61 Hz
 PW1 2.63 usec
 OBNJC 1H
 OBFRC 500.00 MHz
 OBSET 162167.63 Hz
 RGAIN 24
 SCANS 500 times
 SLVNT CD300
 SPINNT 9 Hz
 TEMP 26.5 C

Date : Mon Apr 7 20:54:56 2003
 FileName : gouseyifourStibStoup
 Comment : 1H Line
 SliceHistory :
 EXMODE : non

POINT : 16384 points
 SAMP : 16384 points
 FREQ : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 58.7 usec
 INTVL : 103.0 usec
 TIMES : 512 times
 DUMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.61 Hz
 PH1 : 2.63 usec
 OBNUC : 1H
 OBFREQ : 500.00 MHz
 OBFSET : 162167.63 Hz
 RGAIN : 25

SCANS : 512 times

SLVNT : CD300
 SPINNING : 13 Hz
 TEMP : 26.7 C

1H Line

Date : Tue Apr 15 11:31:16 2003

FileName : gousei\TIPSsucine.nda
 Comment : 1H Line
 SliceHistory :
 EXMODE : non

POINT 16384 points
 SAMPD 16384 points
 FREQU 10000.0 Hz
 FILTR 5000 Hz
 DELAY 40.0 usec
 DEATH 58.7 usec
 INTVL 100.0 usec
 TIMES 64 times
 DUMMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3999 msec
 PREDL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 0.61 Hz
 PW1 2.63 usec
 OBNUC 1H
 OBFRQ 500.00 MHz
 OBSET 162167.63 Hz
 RGAIN 22
 SCANS 64 times
 SLVNT CDCL3
 SPINNING 13 Hz
 TEMP 26.6 C

1H Line

Date : Tue Apr 15 14:29 2003
 FileName : gouseiyu1TPSSupine13C n
 Comment : 1H Line
 SliceHistory :
 EXMODE : bcm
 POINT : 16384 points
 SAMPO : 16384 points
 FREQU : 30030.0 Hz
 FILTR : 15000 Hz
 DELAY : 13.3 usec
 DEQOT : 16.0 usec
 INIYL : 33.3 usec
 TIMES : 1000000 times
 DUMMY : 1 times
 PO : 2.4544 sec
 ACQTM : 545.5872 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 1.83 Hz
 PW1 : 8.00 usec
 13C : 125.65 MHz
 OBFRQ : 127958.00 Hz
 OBSET : 29
 RGAIN : 29
 1H : 500.00 MHz
 IRFRT : 162160.00 Hz
 IRPW : 85.0 usec
 IRPNS : 0
 SCANS : 3244 times
 SLWT : CDCL3
 SPINNING : 11 Hz
 TEMP : 29.1 C

1H Line

Date : Tue Apr 15 14:32:19 2003
FileName : gousei\h1p5supisita.nm
Comment : 1H Line
SliceHistory :
EXMODE : non

POINT 16384 points
SAMPD 16384 points
FREQ 1000.0 Hz
FILTR 5000 Hz
DELT 40.0 usec
DEADT 58.7 usec
INVT 100.0 usec
TIMES 64 times
DUMMY 1 times
PD 5.3616 sec
ACQTM 1638.3999 msec
PREDL 0.01000 msec
INVT 1000.0000 msec
RESOL 0.61 Hz
PHI 2.63 usec
OBNUC 1H
OBPRQ 500.00 MHz
OBSET 162157.63 Hz
RGAIN 23

SCANS 64 times
SLVNT : CDCL3
SPINNING 14 Hz
TEMP 26.9 C

1H Line

Date : Tue Apr 15 18:57:17 2003

FileName : gousei\h1p\sup\stai13C
 Comment : 1H Line
 SliceHistory :
 EXMODE : bcm

POINT : 16384 points
 SAMPO : 16384 points
 FREQ : 30030.0 Hz
 FILTR : 15000 Hz
 DELAY : 13.3 usec
 DEACT : 16.0 usec
 INVL : 33.3 usec
 TIMES : 1000000 times
 DUMMY : 1 times
 PD : 2.4544 sec
 ACQTM : 545.5872 msec
 PREDL : 0.01000 msec
 INVT : 1000.0000 msec
 RESOL : 1.63 Hz
 PWI : 8.00 usec
 OBNUC : 13C
 OBPRQ : 125.65 MHz
 OBSET : 127958.00 Hz
 RGAIN : 28
 IRNUC : 1H
 IRFRQ : 500.00 MHz
 IRSET : 162160.00 Hz
 IRPRQ : 85.0 usec
 IRMS : 0

SCANS : 5269 times

SLVNT : CDCL3
 SPINNT : 13 Hz
 TEMP : 29.1 C

1H Line

Date : Mon Apr 22 21: 05: 34 2002
FileName : LoadingFID.nmdata
Comment : 1H Line
SliceHistory :
EXMODE : non

POINT 16384 points
SAMPD 16384 points
FREQ 10000.0 Hz
FILTR 5000.0 Hz
DELAY 40.0 usec
DEATH 58.7 usec
INTVL 100.0 usec
TIMES 32 times
DUMMY 1 times
PD 5 3616 sec
ACQTM 1638 3999 msec
PREL 0.01000 msec
INWT 1000.0000 msec
RESOL 0.61 Hz
PWL 2.63 usec
OBNUC 1H
OBFRQ 500.00 MHz
ORSET 162167.63 Hz
RGAIN 24

SCANS : 32 times
SLWT : CCCL3
SPINNING : 13 Hz
TEMP : 24.6 C

D:\TBDPS-spiro-ue-13C.als
 COMNT TBDPS-spiro-ue
 DATIM Fri Feb 15 21:31:47 2002
 OBNUC 13C
 EXMOD BCM
 OBFRQ 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 1103
 ACQTM 1.606 sec
 PD 1.394 sec
 PW1 5.0 us
 IIRNUC 1H
 CTEMP 23.5 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 24

1H Line

Date : Wed May 1 16:46:08 2002
 FileName : gouseiyhTBDPSspis:ta3.n
 Comment : 1H Line
 SliceHistory : non
 EXMODE : non

POINT 16384 points
 SAMPD 16384 points
 FREQ 10000.0 Hz
 FILTR 5000 Hz
 DELTA 40.0 usec
 DEADT 58.7 usec
 INTVL 100.0 usec
 TIMES 10000 times
 DUMMY 1 times
 P0 5.3616 sec
 ACQTM 1638.3999 msec
 PREDL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 0.61 Hz
 PW1 2.63 usec
 1H 500.00 MHz
 GBFRQ 162167.63 Hz
 GBSET 27
 SCANS 2340 times

CDCL3
 SLVNT SPINNING 13 Hz
 TEMP 23.2 C

D:\tbds-spiro-sita-deptl.a.s
 COMNT TBDS-spiro-sita-DEPT
 DATIM Sat Feb 16 04:17:54 2002
 OBNUC 13C
 EXMOD BCM
 OBFRO 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 4000
 ACQTM 1.606 sec
 PD 1.394 sec
 PW1 4.0 us
 IRNUC 1H
 CTMP 22.3 C
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 24