Supporting Information

Enantioselective Construction of Octahydroquinolines via Trienamine-Mediated Diels–Alder Reactions

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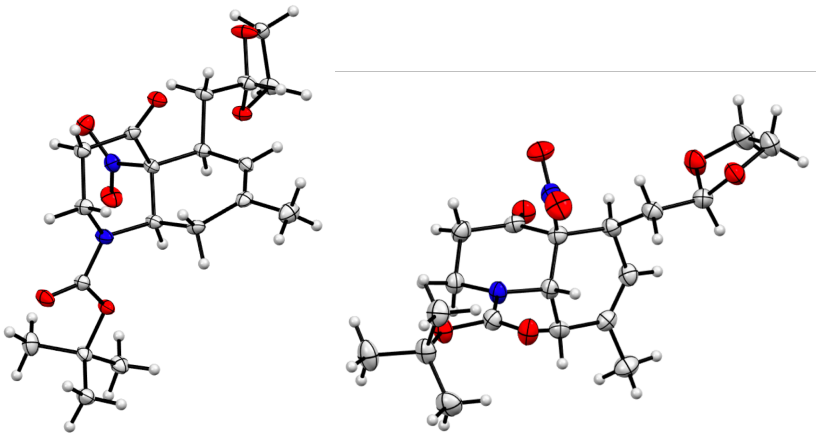
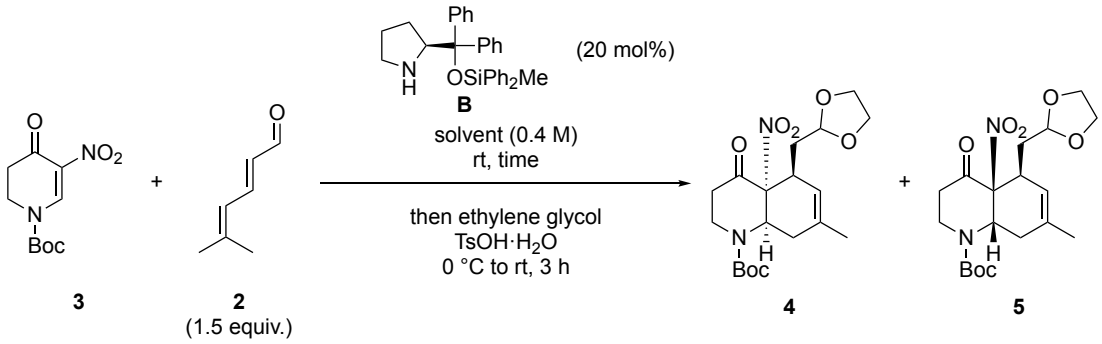
General Remarks: All reactions were monitored by thin-layer chromatography using Merck 60 F254 precoated silica gel plates (0.25 mm thickness). Melting points were measured by Yanagimoto micromelting point apparatus. Specific optical rotations were measured using a JASCO P-1020 polarimeter. FT-IR spectra were recorded on a SHIMADZU IR Affinity-IS. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECX 500 FT-NMR spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR) instrument. Data for ^{1}H NMR are reported as chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doubledoublet, ddd = doubledoubledoublet, dt = doubletriplet, q = quartet, quint. = quintet, m = multiplet, br = broad), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported as chemical shift. X-ray crystallographic analysis: conducted on a Bruker smart APEX-II diffractometer with graphite-monochromated Mo Ka radiation. The high-resolution mass spectra were recorded on a BRUKER impact II. Preparative thin layer chromatography was performed using Wakogel B-5F purchased from Wako Pure Chemical Industries, Tokyo, Japan. Flash chromatography was performed using silica gel 60N of Kanto Chemical Co. Int., Tokyo, Japan and amino silica gel (SiO_2–NH) of Fuji Silysia Co. Int., Japan. HPLC analysis was performed on a SHIMADZU Prominence series, UV detection monitored at appropriate wavelength respectively, using DAICEL Chiralpak IC (0.46 cm × 25 cm) or DAICEL Chiralcel OD-H (0.46 cm × 25 cm).

Figure S1: ORTEP view of compounds **4** and **5**.



ORTEP view of **4** ORTEP view of **5**

Table S1: Solvent screening of catalytic Diels–Alder reaction with 5-nitro-2,3-dihydro-4-pyridone and 5-methyl-2,4-hexadienal in the presence of secondary amine organocatalyst.[a]

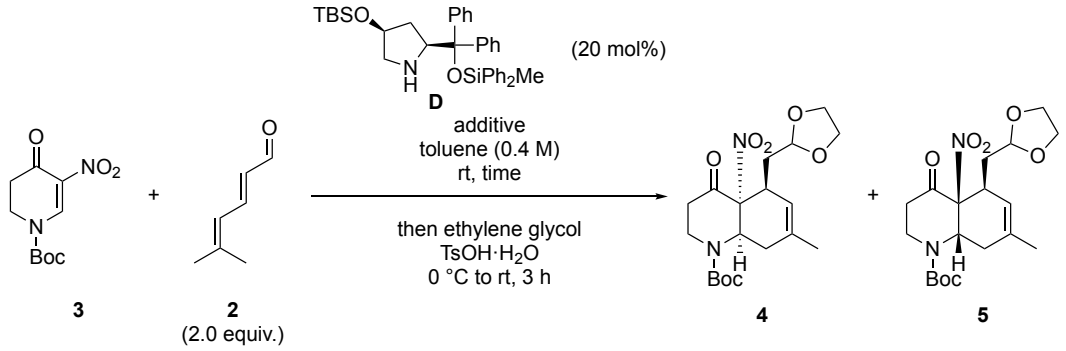


entry	solvent	time	yield (2 steps)	dr[b] **4** : **5**	*ee* of **4**	*ee* of **5**
1	CH_2Cl_2	27 h	66 %	1 : 1	50% *ee*	61% *ee*
2	EtOAc	79 h	58 %	0.9 : 1	81% *ee*	69% *ee*
3	THF	173 h	51 %	0.9 : 1	74% *ee*	61% *ee*
4	DMF	173 h	n.d.	0.7 : 1	52% *ee*	54% *ee*
5	MeOH	164 h	n.d.	0.35 : 1	76% *ee*	64% *ee*
6	MeCN	144 h	n.d.	0.7 : 1	49% *ee*	63% *ee*
7	toluene	19 h	61 %	1.2 : 1	87% *ee*	41% *ee*
8 [c]	toluene	6.5 h	85 %	1.6 : 1	87% *ee*	40% *ee*

n.d.; not determined

[a] Reaction conditions for Diels–Alder reaction: aldehyde **2** (0.15 mmol), 5-nitro-2,3-dihydro-4-pyridone **3** (0.1 mmol), catalyst **B** (0.02 mmol), in toluene (0.25 mL) at 23 °C in open flask; Reaction condition for acetal protection reaction: *p*-toluenesulfonic acid (0.1 mmol) and ethylene glycol (1.5 mmol) at 23 °C for 5 h in one pot. [b] Diastereomeric ratio was determined by ^{1}H-NMR spectra of the crude mixture. [c] 2 equivalents of aldehyde **2** was employed.

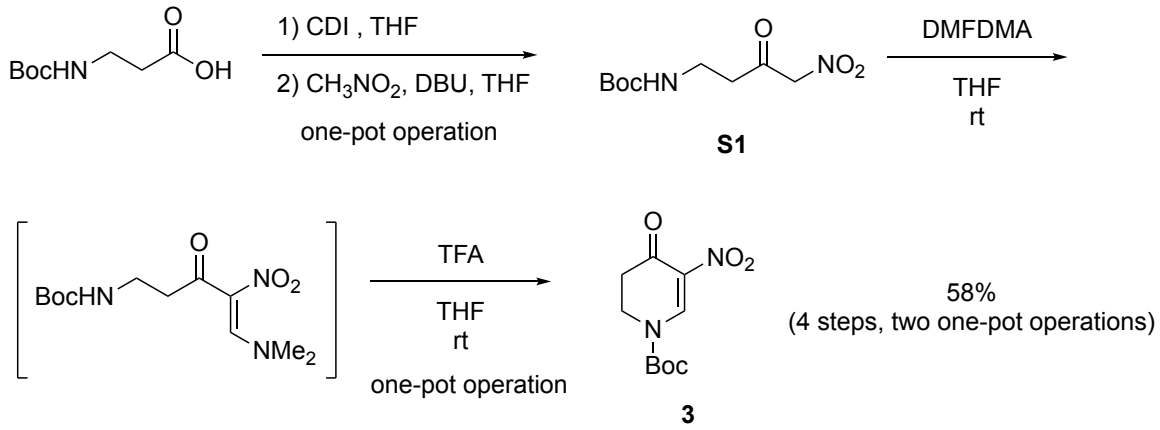
Table S2: Acid screening of catalytic Diels–Alder reaction with 5-nitro-2,3-dihydro-4-pyridone and 5-methyl-2,4-hexadienal in the presence of secondary amine organocatalyst.[a]



entry	adittive (pKa)	equiv. of additive	time	yield	dr[b]	*ee* of major isomer
1	*o*-nitorobenzoic acid (2.17)	100 mol%	> 7 h	29 %	2.6 : 1	95% *ee*
2	*m*-anisic acid (4.09)	100 mol%	3 h	78 %	4.6 : 1	95% *ee*
3	benzoic acid (4.20)	200 mol%	3 h	88 %	4.0 : 1	97% *ee*
4	〃	100 mol%	2.5 h	96 %	4.6 : 1	96% *ee*
5	〃	50 mol%	3 h	83 %	4.7 : 1	95% *ee*
6	〃	20 mol%	3 h	71%	3.7 : 1	95% *ee*
7	acetic acid (4.76)	100 mol%	4.5 h	79 %	4.8 : 1	94% *ee*

[a] Reaction conditions for Diels–Alder reaction: aldehyde **2** (0.2 mmol), 5-nitro-2,3-dihydro-4-pyridone **3** (0.1 mmol), catalyst **D** (0.02 mmol), in toluene (0.25 mL) at 23 °C in open flask; Reaction condition for acetal protection reaction: *p*-toluenesulfonic acid (0.1 mmol) and ethylene glycol (1.5 mmol) at 23 °C for 3 h in one pot. [b] Diastereomeric ratio was determined by ^{1}H-NMR spectra of the crude mixture.

Synthesis of 5-nitro-2,3-dihydropyridone derivative 3



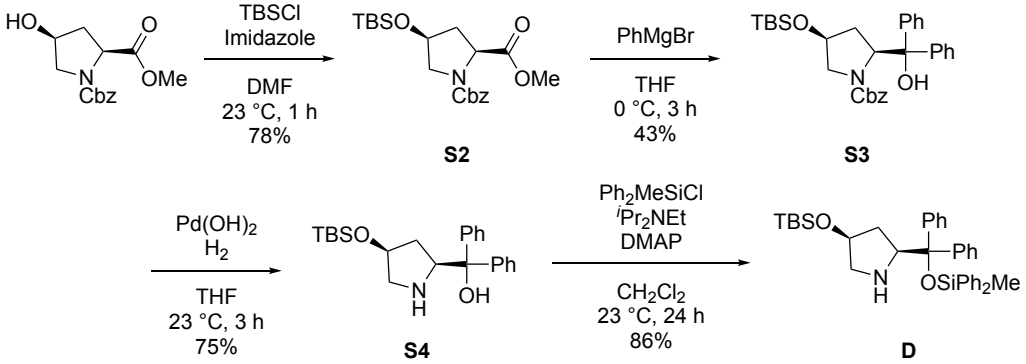
To a solution of *N*-(*tert*-butoxycarbonyl)-β-alanine (3.0 g, 16 mmol) in dry THF (20 mL), 1,1-dicarbonyldiimidazole (CDI, 3.09 g, 19 mmol) was added at at room temperature under Ar atmosphere. The resulting mixture was stirred for 2 h. In another flask, to a solution of DBU (3.70 g, 24 mmol) in dry THF (10 mL), nitromethane (1.3 mL, 24 mmol) was slowly added at room temperature and stirred for 1 h. After 1 h stirred, the reaction mixture of starting material and CDI was slowly added to this activated nitromethane solution at room temperature. After 14 h stirred, the resulting mixture was quenched with 1M aqueous HCl solution at 0 °C and extracted three times with EtOAc. The combined organic phases were washed with brine and dried over $MgSO_4$, and concentrated under reduced pressure. The resulting white solids (**S1**) were directly used to next reaction.

The crude materials of **S1** were dissolved in anhydrous THF (15 mL) and it was added to a solution of *N*,*N*-dimethylformamide dimethyl acetal (DMFDMA, 2.5 mL, 19 mmol) at room temperature under Ar atmosphere. After 15 min stirred at ambient temperature, excess amount of trifluorocaetic acid (TFA, 12 mL, 160 mmol) was slowly added to reaction mixture at 0 °C. The reaction mixture was stirred for additional 2 h at room temperature. The resulting mixture was concentrated under reduced pressure to remove TFA. The crude materials were directly purified by flash chromatography (SiO_2, 50% Et_2O/*n*-hexane). Then, obtained solids were recrystallized with mixed solution of *n*-hexane and dichloromethane. As a result, 5-nitro-2,3-dihydropyridone derivative **3** was obtained as yellow crystal (2.22 g, 58% over 2 pot operation).

5-Nitro-2,3-dihydropyridone derivative **3**

Yellow crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (s, 1H), 4.05 (t, J = 7.5 Hz, 2H), 2.68 (t, J = 7.5 Hz, 2H), 1.56 (s, 9H);^{13}C NMR (125 MHz, $CDCl_3$) δ 181.2, 149.2, 148.6, 127.7, 86.9, 42.4, 35.3, 27.6; IR (neat) ν_{max} 1747, 1695, 1589, 1352, 1273, 1238, 1145, 1118, 1031, 839, 759, cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{10}H_{14}N_2Na_1O_5]^+$: 265.0795, found : 265.0783; mp 118–119 °C.

Synthesis of *cis*-hydroxy proline derivative (catalyst D)



Synthesis of **S2**

To a solution of *N*-Cbz-*cis*-4-hydroxy-L-proline methyl ester (5.72 g, 20.5 mmol) in DMF (20 mL), TBSCl (4.63 g, 30.7 mmol) and imidazole (4.88 g, 71.8 mmol) were added at room temperature under Ar atmosphere. After the reaction mixture was stirred for 1 h, the resulting mixture was quenched with brine. The aqueous layer was extracted three times with EtOAc. To the combined organic layer was washed with cold 2M aqueous HCl solution, saturated brine, and concentrated under reduced pressure. The crude materials were purified by flash chromatography (SiO_2, 14% EtOAc/*n*-hexane) to provide *N*-Cbz-*cis*-4-[(*tert*-butyldimethylsilyl)oxy]-L-proline methyl ester **S2** (6.26 g, 78%) as a colorless amorphous powder. The ^{1}H-NMR of **S2** seems complex mixture, because it is observed as a rotamer mixture. Thus, the structure elucidation was carried out after conversion to **S3**.

Synthesis of **S3**

To a solution of *N*-Cbz-*cis*-4-[(*tert*-butyldimethylsilyl)oxy]-L-proline methyl ester **S2** (1.15 g, 2.92 mmol) in THF (3 mL), 1M phenylmagnesium bromide in THF solution (10 mL, 10 mmol) was slowly added at 0 °C under Ar atmosphere. After the reaction mixture was stirred for 3 h at 0 °C, the resulting mixture was quenched with saturated aqueous NH_4Cl at 0 °C and filtrated with Celite pad. The aqueous layer was extracted three times with EtOAc. The combined organic layer was washed saturated brine and concentrated under reduced pressure. The crude materials were purified by flash chromatography (SiO_2, 10% EtOAc/*n*-hexane) to afford **S3** (0.66 g, 43%) as a white solid.

Benzyl(2*S*,4*S*)-4-((*tert*-butyldimethylsilyl)oxy)-2-(hydroxydiphenylmethyl)pyrrolidine-1-carboxylate (**S3**)

White solid; ^{1}H NMR (500 MHz, DMSO-d_6, VT 90 °C) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.27–7.35 (m, 5H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.07–7.15 (m, 5 H), 5.56 (s, 1H), 5.10 (q, *J* = 4.5 Hz, 1H), 4.87 (d, *J* = 13.0 Hz, 1H), 4.32–4.37 (m, 1H), 3.96 (dd, *J* = 11.0, 7.0 Hz, 1H), 3.21 (q, *J* = 11.0 Hz, 1H), 3.05 (s, 1H), 2.35 (dt, *J* = 14.0, 8.0 Hz, 1H), 1.73 (dt, *J* = 14.0, 4.0 Hz, 1H), 0.85 (s, 9H), 0.06 (s, 3H), 0.00 (s, 3H) ; ^{13}C NMR (125 MHz, DMSO-d_6, VT 90 °C) δ 154.4, 145.9, 145.2, 136.5, 127.7-125.7(15C), 79.7, 69.9, 63.7,

63.5, 55.0, 36.9, 25.1, 17.1, –5.8, –5.5; IR (neat) ν_{max} 3388, 1697, 1411, 1116, 1043, 1014, 893, 837, 752 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{31}H_{39}N_1Na_1O_4Si_1]^+$: 540.2541, found : 540.2514; $[\alpha]^{28}_D$ +118 (*c* 1.9, $CHCl_3$); mp 103–106 °C.

Synthesis of **S4**

To a solution of **S3** (1.49 g, 2.88 mmol) in THF (17 mL), palladium hydroxide (0.15 g, 10 w/w%) was added at ambient temperature. After the reaction mixture was stirred for 3 h under H_2 atmosphere, the resulting mixture was filtrated with Celite pad and amino silica gel pad. The resulting solution was concentrated under reduced pressure. The crude materials were purified by flash chromatography (SiO_2, 50% EtOAc/*n*-hexane) to provide **S4** (0.83 g, 75%) as a white solid.

((2*S*,4*S*)-4-((*tert*-Butyldimethylsilyl)oxy)pyrrolidin-2-yl)diphenylmethanol (**S4**)

White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.26–7.31 (m, 4H), 7.16 (t, *J* = 7.0 Hz, 2H), 4.71 (br. s, 1H), 4.41 (dd, *J* = 9.0, 5.5 Hz, 1H), 4.27–4.30 (m, 1H), 2.96 (d, *J* = 3.0 Hz, 1H), 1.85–1.90 (m, 1H), 1.80 (br. s, 1H), 1.65 (dq, *J* = 14.0, 5.0 Hz, 1H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 146.6, 128.2, 128.0, 126.4, 126.3, 126.2, 125.6, 77.6, 72.5, 64.1, 55.8, 36.7, 25.8, 18.1, –4.9; IR (neat) ν_{max} 3356, 1247, 1110, 1058, 871, 867, 839, 777 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{23}H_{33}N_1Na_1O_2Si]^+$: 406.2173, found : 406.2155; $[\alpha]^{28}_D$ –47 (*c* 0.9, $CHCl_3$); mp 92–95 °C.

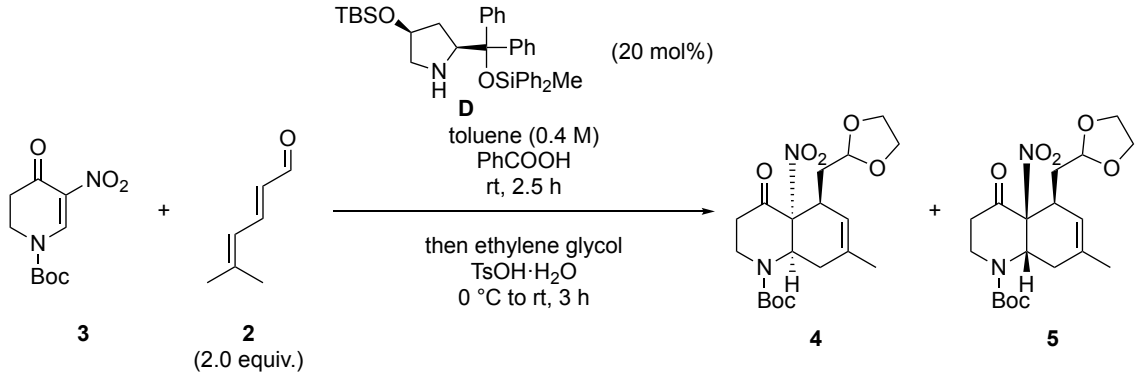
Synthesis of catalyst **D**

To a solution of **S4** (2.57 g, 6.70 mmol) in CH_2Cl_2 (17 mL), chloromethyldiphenylsilane (1.4 mL, 6.7 mmol), ^{i}Pr$_2$NEt$_2$ (2.3 mL, 13 mmol), and *N*,*N*-dimethyl-4-aminopyridine (163 mg, 1.34 mmol) were added at room temperature under Ar atmosphere. After the reaction mixture was stirred for 48 h, the resulting mixture was concentrated under reduced pressure. The crude materials were directly purified by flash chromatography (SiO_2, 10% EtOAc/*n*-hexane) to afford catalyst **D** (2.32 g, 86%) as a colorless oil.

(2*S*,4*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-2-(((methyldiphenylsilyl)oxy)diphenylmethyl)pyrrolidine (catalyst **D**)

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.51 (m, 4H), 7.41–7.44 (m, 2H), 7.33–7.36 (m, 4H), 7.27–7.32 (m, 4H), 7.20–7.24 (m, 6H), 4.17 (br. t, *J* = 6.0 Hz, 1H), 3.90 (br. t, *J* = 8.0 Hz, 1H), 2.78–2.82 (m, 1H), 2.41–2.45 (m, 1H), 1.62–1.74 (m, 3H), 0.81 (s, 9H), 0.24 (s, 3H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0, 144.7, 138.5, 134.4, 134.2, 129.1, 128.8, 127.8, 127.5, 127.4, 127.2, 126.9, 83.7, 72.3, 64.6, 55.1, 37.9, 25.8, 18.0, –1.0, –4.7, –4.8; IR (neat) ν_{max} 3066, 1427, 1251, 1110, 1068, 835, 775 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{36}H_{45}N_1Na_1O_2Si_2]^+$: 602.2881, found : 602.2847; $[\alpha]^{28}_D$ –25 (*c* 0.69, $CHCl_3$).

General procedure of the Diels–Alder reaction using 5-nitro-2,3-dihydropyridone (Table 1, entry 6)



cis-Hydroxy proline derivative **D** (catalyst **D**, 11.6 mg, 0.020 mmol) was added to a solution of 5-nitro-2,3-dihydropyridone **3** (24.2 mg, 0.10 mmol), 5-methylhexa-2,4-dienal (**2**) (22 mg, 0.20 mmol) and benzoic acid (12.2 mg, 0.1 mmol) in toluene (250 μL) at 23 °C in open flask. The reaction mixture was stirred for 2.5 h. To the resulting mixture, ethylene glycol (84 μL, 1.5 mmol) and TsOH·H_2O (21 mg, 0.11 mmol) was added at 0 °C. The reaction mixture was stirred for additional 3 h at room temperature. The resulting mixture was slowly quenched with saturated aqueous NH_4Cl at 0 °C. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layer was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The crude materials were purified by flash chromatography (SiO_2, 12.5% EtOAc/*n*-hexane) to provide major cycloadduct **4** (31.0 mg, 79%) as white solid, and minor cycloadduct **5** (6.7 mg, 17%) as white solid (2 steps, total yield 96%, dr = 4.6 : 1). Recrystallization of **4** and **5** were performed with *n*-hexane and dichloromethane to provide colorless crystals. Enantiomeric excess of major cycloadduct **4** (96% *ee*) and **5** (40% *ee*) were determined by HPLC with ChiralPak IC column. For major isomer **4**: 10% *i*-PrOH/*n*-hexane, 0.5 mL/min; major enantiomer: t_R = 19.1 min, minor enantiomer: t_R = 25.3 min. For minor isomer **5**: 10% *i*-PrOH/*n*-hexane, 0.5 mL/min; major enantiomer: t_R = 21.7 min, minor enantiomer: t_R = 20.2 min.

tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-methyl-4a-nitro-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**4**)

Colorless crystals; ^{1}H NMR (500 MHz, DMSO-d_6, VT 80 °C) δ 4.81 (s, 1H), 4.69 (br. t, *J* = 10.0 Hz, 1H), 4.23 (t, *J* = 4.0 Hz, 1H), 3.93 (br. s, 1H), 3.26 (td, *J* = 12.0, 4.5 Hz, 2H), 3.16 (td, *J* = 12.0, 5.5 Hz, 2H), 2.84–2.89 (m, 1H), 2.36 (br. d, *J* = 8.5 Hz, 1H), 2.28 (quint., *J* = 8.5 Hz, 1H), 1.93 (dt, *J* = 16.0 Hz, 5.0 Hz, 1H), 1.76 (br. dd, *J* = 13.5, 7.5 Hz, 1H), 1.67 (br. d, *J* = 10.0 Hz, 1H), 1.57–1.63 (m, 1H), 1.04 (s, 3H), 0.99 (dd, *J* = 10.0, 4.8 Hz, 1H), 0.84 (s, 9H); ^{13}C NMR (125 MHz, DMSO-d_6, VT 80 °C) δ 196.1, 153.1, 130.2, 121.4, 101.8, 96.5, 80.0, 64.2, 64.9, 55.6, 38.8, 38.1, 36.9, 33.3, 30.2, 27.5, 21.4; IR (neat) ν_{max} 2976, 1736, 1697, 1547, 1406, 1159, 1115 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{28}N_2Na_1O_7]^+$: 419.1789, found : 419.1763;

$[\alpha]^{24}_{D}$ –58 (*c* 0.51, $CHCl_3$); mp 113–117 °C.

tert-Butyl(4a*S*,5*S*,8a*S*)-5-((1,3-dioxolan-2-yl)methyl)-7-methyl-4a-nitro-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**5**)

Colorless crystals; ^{1}H NMR (500 MHz, benzene-d_6, VT 78 ℃) δ 5.62 (s, 1H), 5.50 (br. s, 1H), 4.81–4.84 (m, 1H), 4.03 (br. s, 1H), 3.73–3.77 (m, 1H), 3.39–3.45 (m, 2H), 3.27–3.33 (m, 2H), 2.84–2.90 (m, 1H), 2.29–2.36 (m, 1H), 2.08 (dd, *J* = 18.0, 7.0 Hz, 1H), 1.90–1.95 (m, 1H), 1.63–1.76 (m, 3H), 1.48 (s, 9H), 1.31 (s, 3H);^{13}C NMR (125 MHz, benzene-d_6, VT 78 ℃) δ 194.2, 154.3, 129.6, 122.9, 102.7, 97.4, 80.8, 65.0, 64.8, 51.9, 39.1, 37.3, 36.9, 35.4, 31.1, 28.4, 22.2; IR (neat) ν_{max} 2976, 1738, 1697, 1151, 1395, 1153, 1033 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{28}N_2Na_1O_7]^+$: 419.1789, found : 419.1770; $[\alpha]^{23}_{D}$ +40 (*c* 0.75, $CHCl_3$); mp 143–146 °C; Crystals of **5** were obtained as racemic mixture.

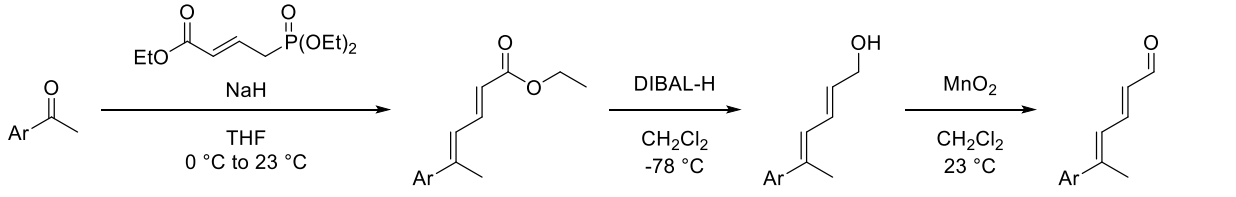
Gram-scale synthesis of 4 (Table 1, entry 8)

Benzoic acid (378.1 mg, 3.01 mmol) was added to a solution of 5-nitro-2,3-dihydropyridone **3** (1.0 g, 4.13 mmol), 5-methylhexa-2,4-dienal (**2**, 902 mg, 8.24 mmol) and catalyst **D** (119 mg, 0.21 mmol) in toluene (15 mL) at 23 °C under Ar atmosphere. The reaction mixture was stirred for 15 h. To the resulting mixture, ethylene glycol (3.46 mL, 61.8 mmol) and $TsOH \cdot H_2O$ (864 mg, 4.5 mmol) was added at 0 °C. The reaction mixture was stirred for additional 5 h at 23 °C. The resulting mixture was slowly quenched with saturated aqueous NH_4Cl at 0 °C. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layer was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The crude materials were purified by flash chromatography (SiO_2, 12.5% EtOAc/*n*-hexane gradient) to provide major cycloadduct **4** (1.18 g, 72%) and minor cycloadduct **5** (266 mg, 16%). Enantiomeric excess of major cycloadduct **4** (96% *ee*) were determined by HPLC with ChiralPak IC column.

Substrate scope; Preparation of substituted 2,4-dienal.

Aldehydes as starting materials of compounds **2**, **7**, **8**, **10**, **14** were prepared by reported protocols[S1), S2), S3), S4), S5)].

General procedure of aldehydes as starting materials to prepare cycloadducts **9**, **11** and **12**.



Ar = 4-NO_2Ph, 3,5-$(CF_3)_2$Ph or 3,5-$(OMe)_2$Ph

Ar = 4-NO_2Ph, 3,5-$(CF_3)_2$Ph or 3,5-$(OMe)_2$Ph **S9**

Ar = 4-NO_2Ph **S5**, 3,5-$(CF_3)_2$Ph **S7** or 3,5-$(OMe)_2$Ph **S10**

Ar = 4-NO_2Ph **S6**, 3,5-$(CF_3)_2$Ph **S8** or 3,5-$(OMe)_2$Ph **S11**

Horner-Wadsworth-Emmons (HWE) Reaction of ketones.

NaH (60% in mineral oil, 1.8 equiv.) was slowly added to solution of triethyl-4-phosphonocrotonate (1.2 equiv.) in THF (0.125 M) at 0 °C under Ar atmosphere. The reaction mixture was stirred for 30 min at room temperature. 4-Nitroacetophenone [or 3,5-bis-(trifluoromethyl)acetophenone or 3,5-dimethoxyacetophenone] (1.0 equiv.) was carefully added to the mixture at 0 °C and the reaction mixture was stirred for 2 h at room temperature. The resulting mixture was quenched with water at 0 °C. The aqueous layer was extracted three times with EtOAc. The combined organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was passed through silica gel pad with $CHCl_3$ and concentrated under reduced pressure. To synthesis of **S5** and **S7**, the crude materials were not purified and directly used to next reduction. To synthesis of **S10**, the crude materials were purified by flash chromatography (SiO_2, 12.5% EtOAc/*n*-hexane) to provide α, β, γ, δ-unsaturated ethyl ester **S9** (14 mmol scale, 33% as *E*/*Z* mixture).

Ethyl-5-(3,5-dimethoxyphenyl)hexa-2,4-dienoate (**S9**) (as *E*/*Z* mixture; see page S29)

Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$,) δ 7.71 (dd, *J* = 15.0, 12.0 Hz), 7.37 (dd, *J* = 15.0, 12.0 Hz), 6.60 (d, *J* = 2.5 Hz), 6.54 (d, *J* = 12.0 Hz), 6.41 (d, *J* = 2.5 Hz), 6.21 (d, *J* = 12.0 Hz), 5.97 (d, *J* = 15.0 Hz), 5.83 (d, *J* = 15.0 Hz), 4.22 (q, *J* = 7.0 Hz), 4.13 (q, *J* = 7.0 Hz), 3.79 (s), 3.77 (s), 2.25 (s), 2.16 (s), 1.30 (t, *J* = 7.0 Hz), 1.23 (t, *J* = 7.0 Hz);^{13}C NMR (125 MHz, $CDCl_3$,) δ 167.2, 167.1, 160.6, 160.5, 148.2, 145.2, 144.1, 142.2, 141.9, 140.3, 125.3, 124.8, 121.4, 120.2, 106.2, 104.5, 104.3, 100.0, 99.7, 60.2, 59.9, 55.2, 25.8, 16.6, 14.2, 14.1; IR (neat) ν_{max} 2937, 1705, 1618, 1585, 1422, 1267, 1204, 1153, 1136, 1043, 977 cm^{-1}; HRMS (ESI) $[M+H]^+$ calculated for $[C_{16}H_{21}O_4]^+$: 277.1434, found : 277.1419.

DIBAL reduction.

DIBAL (1.03 M in hexane, 2.5 equiv.) was slowly added to solution of the crude materials [or purified **S9**] in CH_2Cl_2 (0.3 M) at –78 °C under Ar atmosphere. The reaction mixture was stirred for 1.5 h. The resulting mixture was quenched with EtOAc at –78 °C. After an addition of excess amount of 20% aqueous potassium sodium (+)-tartrate at room temperature, it was stirred for additional 1 h at ambient temperature. The aqueous layer was extracted three times with EtOAc. The combined organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The crude materials were purified by flash chromatography (SiO_2, 20% EtOAc/*n*-hexane) to provide desired allyl alcohols; **S5** (18 mmol scale, 2 steps 45% as *E*/*Z* mixture), and **S10** (4.5 mmol scale, 98% as *E*/*Z* mixture mixture). **S7** was through a silica gel pad, and it was employed as crude materials.

5-(4-Nitrophenyl)hexa-2,4-dien-1-ol (**S5**) (as *E*/*Z* mixture; see page S30)

Yellow solids; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 9.0 Hz), 8.16 (d, *J* = 9.0 Hz), 7.54–7.56 (m), 6.66–

6.71 (m), 6.57–6.60 (d, J = 10.0 Hz), 6.22–6.25 (m), 6.17–6.19 (m), 6.06 (dt, J = 15.0, 6.0 Hz), 5.89 (dt, J = 15.0, 6.0 Hz), 4.30 (d, J = 5.0 Hz), 4.13 (d, J = 6.0 Hz), 2.19 (s), 2.13 (s);^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 146.5, 135.5, 134.2, 133.3, 129.6, 129.1, 128.5, 127.4, 126.9, 126.3, 126.1, 123.6, 123.5, 63.2, 63.1, 24.9, 15.7; IR (neat) ν_{max} 3321, 2998, 1589, 1512, 1336, 1089, 1082, 966 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{12}H_{13}N_1Na_1O_3]^+$: 242.0788, found : 242.0774; mp 56–59 °C.

5-(3,5-Dimethoxyphenyl)hexa-2,4-dien-1-ol (**S10**) (as *E*/*Z* mixture; see page S31)

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61–6.66 (m), 6.58 (d, J = 2.5 Hz), 6.45 (d, J = 11.0 Hz), 6.37–6.38 (m), 6.30–6.35 (m), 6.09 (d, J = 11.0 Hz), 5.93 (dt, J = 15.0, 6.0 Hz), 5.78 (dt, J = 15.0, 6.0 Hz), 4.23 (d, J = 6.0 Hz), 4.08 (d, J = 5.0 Hz), 3.78 (s), 3.76 (s), 2.79 (br. s), 2.12 (s), 2.08 (s);^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 145.0, 143.3, 139.0, 136.2, 132.9, 131.0, 128.7, 127.5, 126.4, 126.3, 106.2, 103.9, 98.9, 98.6, 63.1, 55.1, 25.2, 15.9; IR (neat) ν_{max} 3350, 2935, 1585, 1452, 1421, 1204, 1151, 1064, 1045, 966 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{14}H_{18}Na_1O_3]^+$: 257.1148, found : 257.1142.

Oxidation of allylic alcohol **S5**, **S7**, **S10**.

Manganese (Ⅳ) oxide (10 equiv.) was added to a solution of allyl alcohol **S5** or **S7** (crude materials) or **S10** in CH_2Cl_2 at room temperature under Ar atmosphere. The reaction mixture was stirred for 10 h at ambient temperature. The resulting mixture was filtrated with Celite pad and concentrated under reduced pressure. Flash chromatography (SiO_2, 12.5% EtOAc/*n*-hexane) provided α, β, γ, δ-unsaturated aldehyde **S6** (6.4 mmol scale, 89%), or **S8** (3.2 mmol scale, 29% over three steps), or **S11** (4.3 mmol scale, 99%).

5-(4-Nitrophenyl)hexa-2,4-dienal (**S6**)

Yellow crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (dd, J = 8.0, 2.5 Hz, 1H), 8.21–8.23 (m, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.55 (dd, J = 15.0, 11.5 Hz, 1H), 6.77 (d, J = 11.5 Hz, 1H), 6.32 (qd, J = 8.0, 3.0 Hz, 1H) 2.38 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 147.8, 146.4, 144.9, 133.5, 129.0, 127.7, 126.9, 126.9, 123.8, 16.7; IR (neat) ν_{max} 1662, 1614, 1597, 1506, 1342, 1118, 974, 850 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{12}H_{11}N_1Na_1O_3]^+$: 240.0631, found : 240.0627; mp 129–131 °C.

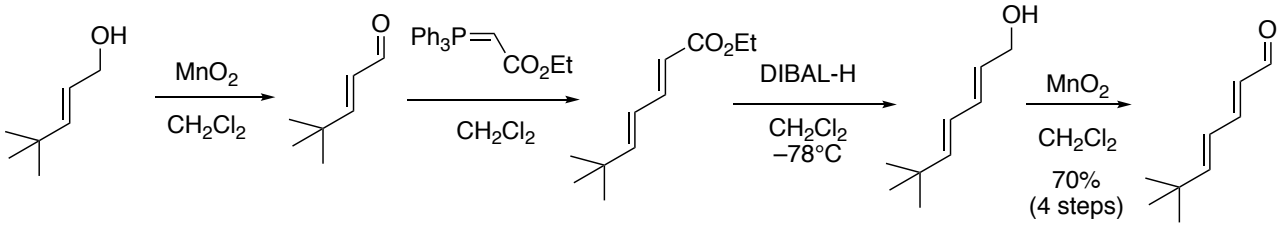
5-(3,5-Bis(trifluoromethyl)phenyl)hexa-2,4-dienal (**S8**)

Pale yellow crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (d, J = 8.0 Hz 1H), 7.92 (s, 2H), 7.84 (s, 1H), 7.55 (dd, J = 15.0, 11.5 Hz, 1H), 6.76 (d, J = 11.5 Hz, 1H), 6.35 (dd, J = 15.0, 8.0 Hz, 1H), 2.40 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$,) δ 193.4, 146.1, 143.9, 143.7, 133.6, 132.0 (q, J = 133.0 Hz), 127.4, 126.1, 126.0, 124.2, 122.1, 16.7; IR (neat) ν_{max} 1674, 1616, 1377, 1271, 1118, 966, 871, 842 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{14}H_{10}F_6Na_1O_1]^+$: 331.0528, found : 331.0528; mp 110–113 °C.

5-(3,5-Dimethoxyphenyl)hexa-2,4-dienal (**S11**)

White solids; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 (d, *J* = 8.0 Hz, 1H), 7.53–7.58 (m, 1H), 6.64–6.70 (m, 3H), 6.47 (s, 1H), 6.26 (dd, *J* = 15.0, 7.0 Hz, 1H), 3.83 (s, 6H), 2.31 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 160.8, 147.8, 143.7, 132.0, 125.1, 106.3, 104.5, 100.6, 554, 16.9; IR (neat) ν_{max} 1660, 1589, 1425, 1205, 1153, 1157, 1120, 974, 833 cm^{-1}; HRMS (ESI) $[M+H]^+$ calculated for $[C_{14}H_{17}O_3]^+$: 233.1172, found : 233.1162; mp 75–80 °C.

Synthesis of **S16**.



S12 **S13** **S14** **S15** **S16**

To a solution of (*E*)-4,4-dimethylpent-2-en-1-ol (**S12**, 773.5 mg, 6.03 mmol)[S6] in CH_2Cl_2 (20 mL), manganese (IV) oxide (5.2g, 60.3 mmol) was added at room temperature. The reaction mixture was stirred for 12 h at room temperature under Ar atmosphere. The resulting mixture was filtrated with Celite pad and concentrated under reduced pressure. The obtained crude materials of **S13** was directly employed to next Wittig reaction.

To a solution of the crude materials of **S13** in CH_2Cl_2 (20 mL), ethyl(triphenylphosphoranylidene)acetate (5.3 g, 15.1 mmol) was added at room temperature. The reaction mixture was stirred for 12 h under Ar atmosphere before removal of CH_2Cl_2 under reduced pressure. The resulting solid was suspended with *n*–hexane/Et_2O (7/1), then it was filtrated with silica-gel pad eluted with *n*–hexane/Et_2O (7/1) to provide 1.23 g of crude materials of **S14**. The obtained crude materials of **S14** was directly employed to next DIBAL-H reduction.

To a solution of the crude materials of **S14** in CH_2Cl_2 (20 mL), DIBAL (1.03M in hexane, 15.1 mL, 15.1 mmol) was added dropwise via syringe at –78 °C under Ar atmosphere. The reaction mixture was stirred for 1.5 h at –78 °C under Ar atmosphere. The resulting mixture was quenched with EtOAc at –78 °C. After an addition of excess amount of 20% aqueous potassium sodium (+)-tartrate at room temperature, it was stirred for additional 1 h at ambient temperature. The aqueous layer was extracted three times with EtOAc. The combined organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The crude materials of **S15** was directly employed to next oxidation.

To a solution of the crude materials of **S15** in CH_2Cl_2 (20 mL), manganese (IV) oxide (5.2g, 60.3 mmol) was

added at room temperature. The reaction mixture was stirred for 14 h at room temperature under Ar atmosphere. The resulting mixture was filtrated with Celite pad and concentrated under reduced pressure. The obtained crude materials were purified by flash chromatography (SiO_2, 5% EtOAc/*n*-hexane) to provide desired aldehyde S16 (643.5 mg, 70%, 4 steps) as pale yellow oil.

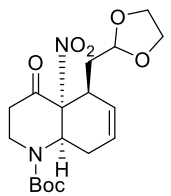
5,6,6-Trimethylhepta-2,4-dienal (**S16**)

Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 15.0, 11.0 Hz, 1H), 6.21 (d, *J* = 11.0 Hz, 1H), 6.11 (dd, *J* = 15.0, 8.0 Hz, 1H), 1.94 (s, 3H) 1.12 (s, 9H);^{13}C NMR (125 MHz, $CDCl_3$,) δ 194.2, 160.7, 149.6, 130.6, 120.4, 37.6, 28.7, 14.2; IR (neat) ν_{max} 2965, 1678, 1620, 1169, 1124, 968, 889 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{10}H_{16}Na_1O_1]^+$: 175.1093, found : 175.1082.

General procedure for substrate scope

Hexa-2,4-dienal (28.8 mg, 0.30 mmol) was added to a solution of 5-nitro-2,3-dihydropyridone **3** (24.2 mg, 0.10 mmol), benzoic acid (12 mg, 0.1 mmol) and catalyst **D** (11.6 mg, 0.020 mmol) in toluene (250 μL) at 23 °C under Ar atmosphere. The reaction mixture was stirred until consumption of 5-nitro-2,3-dihydropyridone **3** monitored by TLC analysis. To the resulting mixture, ethylene glycol (84 μL, 1.5 mmol) and $TsOH\cdot H_2O$ (21 mg, 0.11 mmol) were added at 0 °C. The reaction mixture was stirred for 3 h at 23 °C. The resulting mixture was slowly quenched with saturated aqueous NH_4Cl at 0 °C. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layer was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The crude materials were purified by flash chromatography (SiO_2, 12.5% EtOAc/*n*-hexane) to provide **6** (23.7 mg as separatable diastereomer mixture, 62%) as colorless amorphous powder.

tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-4a-nitro-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**6**)

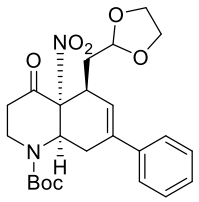


In general procedure; 5 h, yield 62% (0.1 mmol scale, 24 mg), dr = 3 : 1, 91% *ee*. Major diastereomer was separated by flash chromatography (SiO_2, 12% EtOAc/*n*-hexane). Enantiomeric excess was determined by HPLC with ChiralCel IC column. 10% *i*-PrOH/*n*-hexane, 0.5 mL/min; major enantiomer t_R = 23.0 min, minor enantiomer t_R = 29.2 min.

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$, VT 55 °C) δ 5.77 (d, *J* = 10.0 Hz 1H), 5.54 (br. d, *J* = 10.0 Hz, 1H), 5.43 (br. s, 1H), 4.89 (t, *J* = 4.0 Hz, 1H), 4.30 (br. s, 1H), 3.93 (td, *J* = 12.5, 5.0 Hz, 2H), 3.82 (td, *J* = 12.5, 5.5 Hz, 1H), 3.34 (br. s, 9H), 2.99–3.06 (m, 2H), 2.42–2.47 (m, 2H), 2.33–2.38 (m, 1H), 2.21 (br. s, 1H), 1.85 (d, *J* = 13.0 Hz, 2H), 1.50 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, VT 55 °C) δ 196.2, 153.9, 128.8, 121.8, 103.1, 97.5, 81.4, 65.1, 64.9, 56.4, 39.4, 39.1, 38.0, 33.5, 28.3, 26.0; IR (neat) ν_{max} 2978, 1734, 1697, 1547, 1406,

1365, 1157, 1115 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{18}H_{26}N_2Na_1O_7]^+$: 405.1632, found : 405.1608; $[\alpha]^{27}_D$ –42 (*c* 1.0, $CHCl_3$).

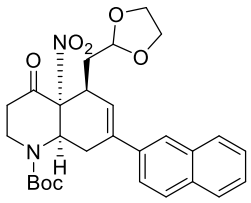
tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-4a-nitro-4-oxo-7-phenyl-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**7**)



5-Phenylhexa-2,4-dienal was used as diene in general procedure; reaction was performed at 0 °C, 36 h, yield 74% (0.1 mmol scale, 34 mg), dr = 10 : 1, 95% *ee*. Major diastereomer was separated by flash chromatography (SiO_2, 11% EtOAc/*n*-hexane). Enantiomeric excess was determined by HPLC with ChiralCel IC column. 10% *i*-PrOH/*n*-hexane, 0.5 mL/min; major enantiomer t_R = 18.4 min, minor enantiomer t_R = 23.3 min.

Pale yellow oil; ^{1}H NMR (500 MHz, benzene-d_6, VT 78 °C) δ 7.08–7.12 (m, 5H), 6.18 (s, 1H), 5.79 (br. s, 1H), 4.72–4.76 (m, 1H), 4.08 (br. s, 1H), 3.39–3.48 (m, 2H), 3.24–3.32 (m, 3H), 2.93 (br. s, 1H), 262–2.75 (m, 3H), 2.27 (br. t, *J* = 14.0 Hz, 1H), 2.18 (dd, *J* = 15.0, 2.0 Hz, 1H), 1.98 (br. d, *J* = 15.0 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, benzene-d_6, VT 78 °C) δ 196.0, 154.1, 140.1, 132.9, 128.7, 126.2, 126.2, 125.9, 103.5, 97.8, 81.1, 65.1, 64.8, 57.7, 40.3, 39.4, 38.1, 34.5, 29.0, 28.3; IR (neat) ν_{max} 2976, 1734, 1697, 1549, 1406, 1366, 1159, 1117 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{24}H_{30}N_2Na_1O_7]^+$: 481.1945, found : 481.1931; $[\alpha]^{27}_D$ –73 (*c* 1.5, $CHCl_3$).

tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-(naphthalen-2-yl)-4a-nitro-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**8**)

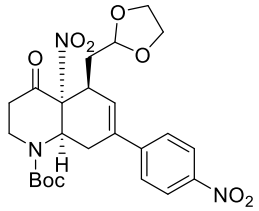


5-(Naphthalen-2-yl)hexa-2,4-dienal was used as diene in general procedure; 5 h, yield 73% (0.1 mmol scale, 37 mg), dr = 7.8 : 1, 95% *ee*. Major diastereomer was separated by flash chromatography (SiO_2, 11% EtOAc/*n*-hexane). Enantiomeric excess was determined by HPLC with ChiralCel IC column. 10% *i*-PrOH/*n*-hexane, 0.5 mL/min; major enantiomer t_R = 24.0 min, minor enantiomer t_R = 33.8 min.

Colorless oil ; ^{1}H NMR (500MHz, benzene-d_6, VT 78 ℃) δ 7.61 (d, *J* = 7.0 Hz, 2H), 7.56–7.58 (m, 2H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.23–7.29 (m, 2H), 6.36 (s, 1H), 5.87 (br. s, 1H), 4.78 (t, *J* = 4.0 Hz, 1H), 4.12 (br. s, 1H), 3.41–3.47 (m, 3H), 3.28–3.32 (m, 2H), 2.97 (br. t, *J* = 12.0 Hz, 1H), 2.87 (br. d, *J* = 15.0 Hz, 1H), 2.69–2.78 (m, 2H), 2.41 (t, *J* = 14.0 Hz, 1H), 2.24 (dt, *J* = 15.0, 2.0 Hz, 1H), 1.99–2.03 (m, 1H), 1.47 (s, 9H); ^{13}C NMR (125MHz, benzene-d_6, VT 78 ℃) δ 196.0, 154.1, 137.3, 134.1, 133.6, 132.8, 128.5, 127.0, 126.9, 126.5, 126.3, 124.7, 124.6, 124.3, 103.6, 97.9, 81.2, 65.1, 64.8, 57.3, 40.4, 39.4, 38.2, 34.5, 29.0, 28.4; IR (neat) ν_{max} 2976, 1734, 1697, 1558, 1549, 1406, 1363, 1219, 1159 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for

$[C_{28}H_{32}N_2Na_1O_7]^+$: 531.2102, found : 531.2079; $[\alpha]^{28}_D$ –92 (*c* 0.4, $CHCl_3$).

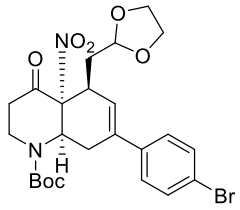
tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-4a-nitro-7-(4-nitrophenyl)-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**9**)



5-(4-Nitrophenyl)hexa-2,4-dienal was used as diene in general procedure; 2.5 mL of toluene was employed. 18 h, yield 71% (0.1 mmol scale, 36 mg), dr = 9.5 : 1, 97% *ee*. Major diastereomer was separated by flash chromatography (SiO_2, 12% EtOAc/*n*-hexane). Enantiomeric excess was determined by HPLC with ChiralCel IC column. 40% *i*-PrOH/*n*-hexane, 0.5 mL/min; major enantiomer t_R = 34.2 min, minor enantiomer t_R = 41.4 min.

Colorless oil; ^{1}H NMR (500 MHz, benzene-d_6, VT 78 °C) δ 7.82 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.17 (s, 1H), 5.75 (br. s, 1H), 4.71 (t, *J* = 3.0 Hz, 1H), 4.08 (br. s, 1H), 3.42–3.49 (m, 2H), 3.27–3.34 (m, 3H), 2.95 (br. t, *J* = 12.0 Hz, 1H), 2.69–2.75 (m, 1H), 2.50–2.61 (m, 2H), 2.08–2.17 (m, 2H), 1.97–2.01 (m, 1H) 1.46 (s, 9H); ^{13}C NMR (125 MHz, benzene-d_6, VT 78 °C) δ 196.0, 154.0, 147.8, 145.3, 131.1, 129.9, 126.1, 123.7, 103.3, 97.6, 81.5, 65.2, 64.9, 56.9, 40.1, 39.5, 38.1, 34.1, 28.3(2C) ; IR (neat) ν_{max} 2980, 1734, 1697, 1595, 1549, 1516, 1406, 1341, 1159, 1111 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{24}H_{29}N_3Na_1O_9]^+$: 526.1796, found : 526.1774; $[\alpha]^{28}_D$ –72 (*c* 1.9, $CHCl_3$).

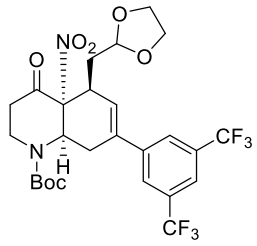
tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-(4-bromophenyl)-4a-nitro-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**10**)



5-(4-Bromophenyl)hexa-2,4-dienal was used as diene in general procedure; 4 h, yield 84% (0.1 mmol scale, 45 mg), dr = 4.6 : 1, 95% *ee*. Major diastereomer was separated by flash chromatography (SiO_2, 9% EtOAc/*n*-hexane). Enantiomeric excess was determined by HPLC with ChiralCel IC column. 10% *i*-PrOH/*n*-hexane, 0.5 mL/min; major enantiomer t_R = 21.9 min, minor enantiomer t_R = 27.4 min.

Pale yellow oil ; ^{1}H NMR (500MHz, benzene-d_6, VT 78 °C) δ 7.22 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.09 (s, 1H), 5.75 (br. s, 1H), 4.71–4.73 (m, 1H), 4.08 (br. s, 1H), 3.40–3.47 (m, 2H), 3.27–3.33 (m, 3H), 2.92 (br. t, *J* = 12.0 Hz, 1H), 2.71 (dt, *J* = 15.0, 9.0 Hz, 1H), 2.55–2.64 (m, 2H), 2.11–2.18 (m, 2H), 1.95–2.00 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (125MHz, benzene-d_6, VT 78 °C) δ 195.9, 154.0, 138.8, 131.8, 131.7, 127.4, 126.9, 122.0, 103.4, 97.7, 81.3, 65.1, 64.8, 57.1, 40.2, 39.4, 38.1, 34.3, 28.6, 28.3; IR (neat) ν_{max} 2978, 1734, 1695, 1547, 1404, 1365, 1157, 1009 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{24}H_{29}Br_1N_2Na_1O_7]^+$: 559.1050, found : 559.1034; $[\alpha]^{28}_D$ –73 (*c* 1.4, $CHCl_3$).

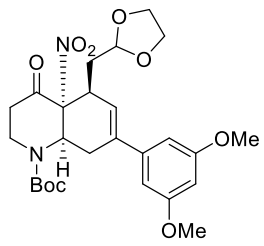
tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-(3,5-bis(trifluoromethyl)phenyl)-4a-nitro-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**11**)



5-(3,5-Bis(trifluoromethyl)phenyl)hexa-2,4-dienal was used as diene in general procedure; 11 h, yield 68% (0.1 mmol, 40 mg), dr = 4.5 : 1, 91% *ee*. Major diastereomer was separated by flash chromatography (SiO_2, 12% EtOAc/*n*-hexane). Enantiomeric excess was determined by HPLC with ChiralCel IC column. 2% *i*-PrOH/*n*-hexane, 0.2 mL/min; major enantiomer t_R = 23.4 min, minor enantiomer t_R = 25.8 min.

Colorless oil ; ^{1}H NMR (500MHz, benzene-d_6, VT 78 °C) δ 7.68 (s, 1H), 7.50 (s, 2H), 6.18 (s, 1H), 5.77 (br. s, 1H), 4.66 (t, *J* = 3.0 Hz, 1H), 4.07 (br. s, 1H), 3.38–3.45 (m, 2H), 3.22–3.31 (m, 3H), 2.87–2.80 (m, 1H), 2.67–2.74 (m, 1H), 2.53–2.58 (m,1H), 2.45 (br. d, *J* = 17.0 Hz, 1H), 2.12–2.17 (m, 2H), 1.92–1.97 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (125MHz, benzene-d_6, VT 78 °C) δ 196.0, 153.9, 142.3, 132.4 (q, *J* = 134.0 Hz), 130.3, 125.7, 125.0, 122.8, 121.4, 103.2, 97.6, 81.6, 65.1, 64.9, 56.8, 40.1, 39.5, 38.1, 33.9, 28.3, 28.2; IR (neat) ν_{max} 2980, 1734, 1699, 1551, 1277, 1165, 1126 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{26}H_{28}F_6N_2Na_1O_7]^+$: 617.1693, found : 617.1677; $[\alpha]^{24}_D$ –62 (c 0.33, $CHCl_3$).

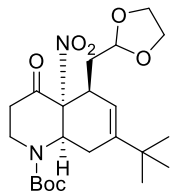
tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-(3,5-dimethoxyphenyl)-4a-nitro-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**12**)



5-(3,5-Dimethoxyphenyl)hexa-2,4-dienal was used as diene in general procedure; 4 h, yield 78% (0.1 mmol scale, 36 mg), dr = 5 : 1, 94% *ee*. Major diastereomer was separated by flash chromatography (SiO_2, 3 to 12% EtOAc/*n*-hexane gradient). Enantiomeric excess was determined by HPLC with ChiralCel IC column. 20% *i*-PrOH/*n*-hexane, 0.5 mL/min; major enantiomer t_R = 23.4 min, minor enantiomer t_R = 28.5 min.

Pale yellow oil,; ^{1}H NMR (500 MHz, $CDCl_3$, VT 55 °C) δ 6.46 (s, 2H), 6.40 (s, 1H), 6.11 (s, 1H), 5.58 (br. s, 1H), 4.95 (t, *J* = 4.0 Hz, 1H), 4.36 (br. s, 1H), 3.95 (td, *J* = 12.5, 5.0 Hz, 2H), 3.80–3.87 (m, 8H), 3.40 (br. s, 1H), 3.21 (br. d, *J* = 10.0 Hz, 1H), 3.05 (dt, *J* = 16.0, 9.0 Hz, 1H), 2.83 (br. s, 1H), 2.42–2.58 (m, 3H), 1.93 (br. d, *J* = 15.0 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, VT 55 °C) δ 196.2, 161.0, 154.0, 141.6, 132.4, 125.8, 104.2, 103.1, 99.7, 97.3, 81.6, 65.2, 64.9, 56.8, 55.5, 39.6, 39.0, 38.1, 33.7, 28.5, 28.3; IR (neat) ν_{max} 2976, 1734, 1697, 1591, 1549, 1408, 1366, 1204, 1153, 1064 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{26}H_{34}N_2Na_1O_9]^+$: 541.2157, found : 541.2124; $[\alpha]^{27}_D$ –64 (*c* 0.61, $CHCl_3$).

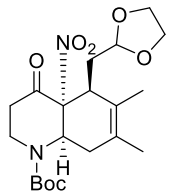
tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-(tert-butyl)-4a-nitro-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**13**)



5,6,6-Trimethylhepta-2,4-dienal was used as diene in general procedure; 32 h, yield 52% (0.1 mmol scale, 23 mg), dr = 2.8 : 1, 92% *ee*. Major diastereomer was separated by flash chromatography (SiO_2, 10 to 12% EtOAc/*n*-hexane gradient). Enantiomeric excess was determined by HPLC with ChiralCel IC column. 10% *i*-PrOH/*n*-hexane, 0.5 mL/min; major enantiomer t_R = 13.9 min, minor enantiomer t_R = 20.2 min.

Colorless oil ; ^{1}H NMR (500 MHz, benzene-d_6, VT 78 °C) δ 5.67 (s, 1H), 5.64 (br. s, 1H), 4.75 (t, *J* = 4.0 Hz, 1H), 4.06 (br. s, 1H), 3.43 (td, *J* = 13.5, 6.0 Hz, 2H), 3.23–3.31 (m, 3H), 3.00–3.05 (m, 1H), 2.65–2.72 (m, 1H), 2.56–2.61 (m, 1H), 2.43 (br. d, *J* = 18.0 Hz, 1H), 2.18 (dd, *J* = 10.0, 3.0 Hz, 1H), 1.96–2.03 (m, 2H), 1.44 (s, 9H), 0.89 (s, 9H); ^{13}C NMR (125 MHz, benzene-d_6, VT 78 °C) δ 196.0, 154.2, 141.3, 121.1, 103.6, 98.1, 80.1, 65.1, 64.8, 57.5, 40.1, 39.5, 38.1, 35.0, 34.8, 28.9, 28.4, 26.5; IR (neat) ν_{max} 2967, 1736, 1697, 1546, 1406, 1392, 1366, 1159, 983 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{22}H_{34}N_2Na_1O_7]^+$: 461.2258, found : 461.2229; $[\alpha]^{28}_D$ –33 (*c* 0.50, $CHCl_3$).

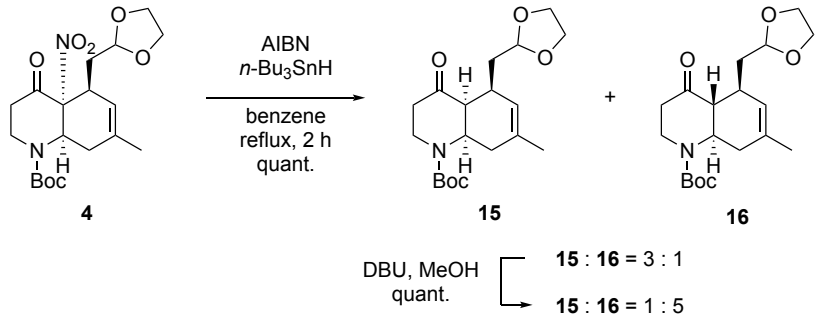
tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-6,7-dimethyl-4a-nitro-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**14**)



4,5-Dimethylhexa-2,4-dienal was used as diene in general procedure; 5 h, yield 71% (0.1 mmol, 29 mg), dr = 3.5 : 1, 90% *ee*. Major diastereomer was separated by flash chromatography (SiO_2, 1 to 13% EtOAc/*n*-hexane gradient). Enantiomeric excess was determined by HPLC with ChiralCel OD-H column. 10% *i*-PrOH/*n*-hexane, 0.5 mL/min; major enantiomer t_R = 13.6 min, minor enantiomer t_R = 15.8 min.

Colorless oil ; ^{1}H NMR (500MHz, benzene-d_6, VT 78 °C) δ 5.46 (t, *J* = 10.0 Hz, 1H), 4.76–4.78 (m, 1H), 4.05 (br. s, 1H), 3.43–3.50 (m, 2H), 3.13–3.28 (m, 2H), 3.12 (br. s, 1H), 2.88–2.94 (m, 1H), 2.70–2.77 (m, 1H), 2.53 (ddd, *J* = 16.0, 7.0, 4.0 Hz, 1H), 2.23 (dq, *J* = 16.0, 2.5 Hz, 1H), 1.94–2.06 (m, 2H), 1.85–1.90 (m, 1H), 1.61 (s, 3H), 1.45 (s, 9H), 1.29 (s, 3H); ^{13}C NMR (125MHz, benzene-d_6, VT 78 °C) δ 196.5 154.1, 127.3, 122.9, 103.8, 99.4, 80.8, 65.0, 64.9, 56.7, 42.9, 38.0, 33.4, 32.5, 28.4, 28.3, 19.2, 16.1; IR (neat) ν_{max} 2978, 2887, 1734, 1697, 1549, 1408, 1365, 1159, 1033 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{20}H_{30}N_2Na_1O_7]^+$: 433.1945, found : 433.1924; $[\alpha]^{24}_D$ –82 (*c* 0.3, $CHCl_3$).

Derivatization of cycloadduct 4 toward total synthesis of *Lycopodium* alkaloids (Scheme 1).



Denitration of cycloadduct **4**.

Tributyltin hydride (429 μL, 0.42 mmol) was added to a solution of cycloadduct **4** (161 mg, 0.41 mmol) and azobisisobutyronitrile (AIBN, 20.2 mg, 0.12 mmol) in benzene (4.06 mL) at room temperature under Ar atmosphere. The reaction mixture was stirred for 2 h at 80 °C under Ar atmosphere. After cooling to room temperature, the resulting mixture was concentrated under reduced pressure. The crude materials was purified by flash chromatography (SiO_2, 20% EtOAc/*n*-hexane) to provide compound **15** and **16** as diastereomer mixture (143 mg, quant., dr = 3 : 1). These diastereomers could be partially separated by careful flash chromatography (SiO_2, 17% EtOAc/*n*-hexane).

Isomerization of from **15** to **16**.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 89 µL, 0.58 mmol) was added to a solution of the diastereomer mixture of **15** and **16** (102 mg, 0.29 mmol) in MeOH (1 mL) at room temperature under Ar atmosphere. The reaction mixture was stirred for 24h at room temperature. The resulting mixture was quenched with saturated aqueous NH_4Cl solution. The aqueous layer was extracted three times with EtOAc. The combined organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The crude mixture was purified by flash chromatography (SiO_2, 20% EtOAc/*n*-hexane) to provide compound **15** and **16** as diastereomer mixture (102 mg, quant., dr = 1 : 5).

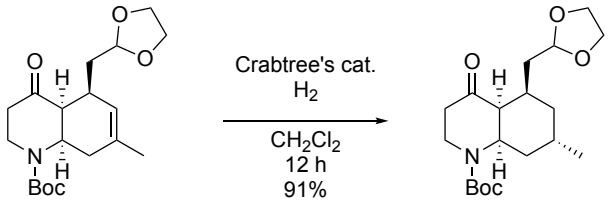
tert-Butyl(4a*S*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-methyl-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**15**)

Colorless oil, ^{1}H NMR (500 MHz, benzene-d_6, VT 78 °C) δ 5.34 (s, 1H), 4.82 (br. s, 1H), 4.81 (t, J = 5.0 Hz, 1H), 4.00 (br. s, 1H), 3.52–3.56 (m, 2H), 3.37–3.42 (m, 2H), 3.20–3.25 (m, 1H), 2.90 (t, J = 5.0 Hz, 1H), 2.52 (br. s, 1H), 2.35 (ddd, J = 14.3, 7.3, 5.5 Hz, 1H), 2.21 (ddd, J = 14.0, 7.0, 4.5 Hz, 1H),2.03–2.13 (m, 2H), 1.95 (dt, J = 14.0, 4.5 Hz, 1H), 1.80 (br. t, J = 14.5 Hz, 1H), 1.46 (s, 12 H); ^{13}C NMR (125 MHz, benzene-d_6, VT 78 °C) δ 205.8, 154.6, 129.8, 125.1, 104.9, 79.8, 64.83, 64.78, 54.9, 51.4, 41.1(2C), 36.7, 34.2, 31.9, 28.6, 22.9; IR (neat) ν_{max} 2972, 2886, 1721, 1688, 1393, 1364, 1157 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{29}N_1Na_1O_5]^+$: 374.1938, found : 374.1923; $[\alpha]^{27}_D$ –16 (*c* 2.2, $CHCl_3$).

tert-Butyl(4a*R*,5*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-methyl-4-oxo-3,4,4a,5,8,8a-hexahydroquinoline-1(2H)-carboxylate (**16**)

Colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (s, 1H), 4.91 (dd, *J* = 5.5, 4.0 Hz, 1H), 4.27 (q, *J* = 7.0 Hz, 1H), 3.90–3.94 (m, 2H), 3.75–3.85 (m, 3H), 3.53–3.59 (m, 1H), 2.77–2.81 (m, 2H), 2.51–2.59 (m, 1H), 2.40–2.45 (m, 2H), 2.12 (dd, *J* = 16.0, 11.0 Hz, 1H), 1.82–1.86 (m, 1H), 1.69–1.75 (m, 4H), 1.45 (s, 9H); ^{1}H NMR (500MHz, DMSO-d_6) δ 4.57 (s, 1H), 4.01 (t, *J* = 4.8 Hz, 1H), 3.19 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.99–3.05 (m, 2H), 2.87–2.94 (m, 2H), 2.73–2.83 (m, 2H), 2.04 (t, *J* = 11.0 Hz, 1H), 1.73 (br. s, 1H), 1.63–1.67 (m, 1H), 1.44–1.51 (m, 2H), 1.31–1.36 (m, 1H), 0.96 (dt, *J* = 13.5, 4.0 Hz, 1H), 0.81 (s, 3H), 0.55–0.68 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.7, 154.4, 132.0, 124.1, 103.3, 80.2, 64.8, 64.4, 54.9, 51.5, 41.5, 38.1, 37.7, 36.3, 32.0, 28.4, 23.4; IR (neat) ν_{max} 2972, 1722, 1688, 1404, 1366, 1169, 1144 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{29}N_1Na_1O_5]^+$: 374.1938, found : 374.1925; $[\alpha]^{27}_D$ –105 (*c* 0.38, $CHCl_3$).

Stereoselective reduction of **15**.



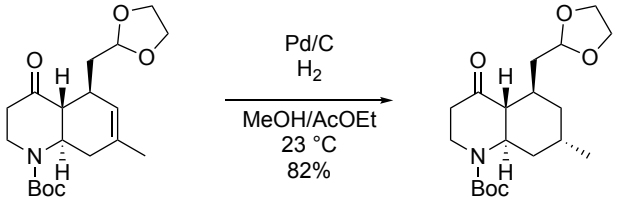
15 **17**

Crabtree's catalyst (1.7 mg, 0.002 mmol) was added to a solution of compound **15** (14 mg, 0.04 mmol) in CH_2Cl_2 (1.33 mL) at room temperature under Ar atmosphere. The reaction mixture was stirred for 12 h under H_2 atmosphere. The resulting mixture was directly concentrated under reduced pressure and purified by flash chromatography (SiO_2, 25% EtOAc/*n*-hexane) to afford compound **17** (13 mg, 91%) as colorless oil.

tert-Butyl(4a*S*,5*R*,7*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-methyl-4-oxooctahydroquinoline-1(2H)-carboxylate (**17**)

Colorless oil; ^{1}H NMR (500 MHz, benzene-d_6, VT 78 °C) δ 4.70 (br. s, 1H), 4.80 (br. t, *J* = 5.0 Hz, 1H), 4.01 (br. s, 1H), 3.50–3.57 (m, 2H), 3.35–3.41 (m, 2H), 3.10 (br. t, *J* = 12.5 Hz, 1H), 2.80 (br. s, 1H), 2.22–2.27 (m, 1H), 1.90–2.11 (m, 6H), 1.38–1.47 (m, 11H), 1.29 (br. d, *J* = 13.0 Hz, 1H), 0.99 (d, *J* = 7.5 Hz, 3H); ^{1}H NMR (500MHz, pyridine-d_5, VT 95 °C) δ 4.89 (t, *J* = 4.0 Hz, 1H), 4.72 (br. s, 1H), 4.13–4.17 (m, 1H), 3.74–3.81 (m, 2H), 3.61–3.68 (m, 2H), 3.30–3.36 (m, 1H), 3.02 (br. s, 1H), 2.39–2.45 (m, 1H), 2.17–2.23 (m, 1H), 2.13 (dt, *J* = 14.0, 4.0 Hz, 1H), 1.99–2.06 (m, 3H), 1.94 (td, *J* = 13.0, 4.7 Hz, 1H), 1.44–1.51 (m, 11H), 1.31 (br. d, *J* = 13.5 Hz, 1H), 1.00 (d, *J* = 7.0 Hz, 3H);^{13}C NMR (125 MHz, benzene-d_6, VT 78 °C) δ 207.7, 154.5, 104.8, 79.6, 64.9, 64.8, 53.0, 52.7, 41.7, 40.5, 38.1, 33.4, 30.3, 28.7, 28.6, 28.2; IR (neat) ν_{max} 2922, 2880, 1715, 1687, 1393, 1364, 1159, 1122 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{31}N_1Na_1O_5]^+$: 376.2094, found :

376.2078; $[\alpha]^{28}_{D}$ +3.3 (*c* 1.3, $CHCl_3$).

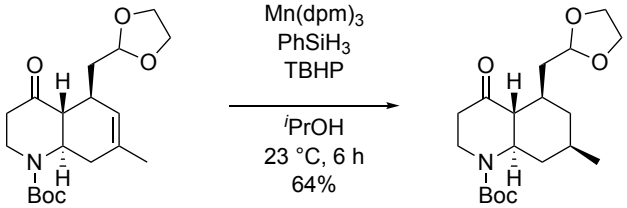


16 **18**

Pd/C (2 mg, 10 w/w%) was added to a solution of compound **16** (20 mg, 0.04 mmol) in MeOH/AcOEt (1 : 1, 1.2 mL) at room temperature under Ar atmosphere. The reaction mixture was stirred for 6 h at room temperature under H_2 atmosphere. The resulting mixture was filtrated with amino silica pad and concentrated under reduced pressure. Flash chromatography (SiO_2, 20% EtOAc/*n*-hexane) provided compound **18** (16 mg, 82%) as colorless crystals.

tert-Butyl(4a*R*,5*R*,7*S*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-methyl-4-oxooctahydroquinoline-1(2H)-carboxylate (**18**)

Colorless crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.98 (dd, *J* = 6.0, 4.5 Hz, 1H), 4.25–4.29 (dd, *J* = 14.0, 6.5 Hz, 1H), 3.90–3.95 (m, 2H), 3.78–3.84 (m, 2H), 3.74 (td, *J* = 12.0, 3.5Hz, 1H), 3.57 (ddd, *J* = 14.0, 12.0, 5.0 Hz, 1H), 2.59 (t, *J* = 11.5 Hz, 1H), 2.50–2.57 (m, 1H), 2.37 (dd, *J* = 18.0, 4.5 Hz, 1H), 2.10–2.18 (m, 2H), 2.04 (br. d, *J* = 11.5 Hz, 1H), 1.93 (ddd, *J* = 14.0, 4.5, 3.0 Hz, 1H), 1.73–1.77 (m, 1H), 1.54–1.63 (m, 2H), 1.39–1.46 (m, 10H), 1.04 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.2, 154.5, 103.3, 80.0, 64.8, 64.4, 55.4, 53.7, 41.9, 38.3, 37.7, 37.3, 37.0, 28.4, 27.5, 27.4, 18.2; IR (neat) ν_{max} 2922, 1707, 1693, 1396, 1364, 1168, 1139 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{31}N_1Na_1O_5]^+$: 376.2094, found : 376.2084; $[\alpha]^{27}_{D}$ –91 (c 0.3, $CHCl_3$); mp 102–104 °C.



16 **19**

Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)manganese (III) (4.8 mg, 0.006 mmol) was added to a solution of compound **16** (20 mg, 0.04 mmol), phenylsilane (8 μL, 0.05 mmol) and TBHP (in decane solution, 15.6 μL, 0.06 mmol) in ^{i}PrOH (284 μL) which was carefully degassed by Ar bubbling, at room temperature under Ar atmosphere. The reaction mixture was stirred for 6 h at room temperature. The resulting mixture was filtrated with amino silica pad and concentrated under reduced pressure. Flash chromatography (SiO_2, 17% EtOAc/*n*-

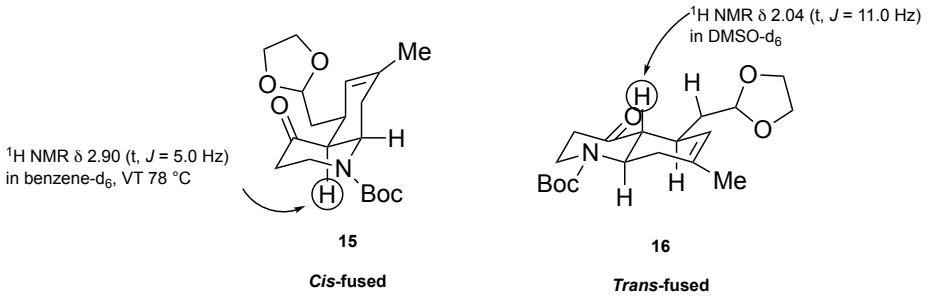
hexane) provided compound **19** (13 mg, 64%) as white solid.

tert-Butyl(4a*R*,5*R*,7*R*,8a*R*)-5-((1,3-dioxolan-2-yl)methyl)-7-methyl-4-oxooctahydroquinoline-1(2H)-carboxylate (**19**)

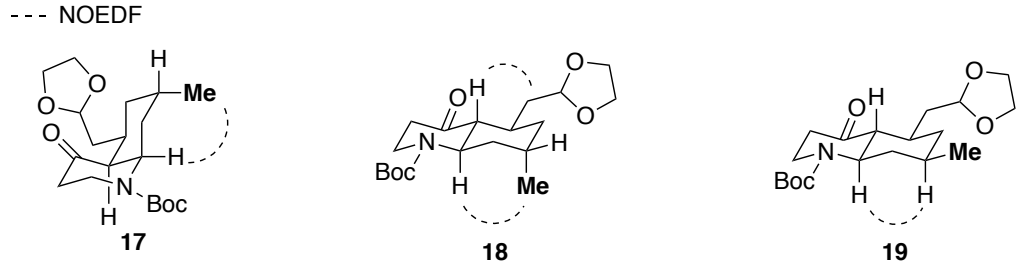
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.99 (dd, *J* = 6.0, 4.5 Hz, 1H), 4.23 (dd, *J* = 14.0, 7.0 Hz, 1H), 3.89–3.98 (m, 2H), 3.78–3.85 (m, 2H), 3.59 (ddd, *J* = 14.5, 12.0, 5.0 Hz, 1H), 3.48 (td, *J* = 11.5, 3.5 Hz, 1H), 2.57 (t, *J* = 11.0 Hz, 1H), 2.47–2.55 (m, 1H), 2.36 (dd, *J* = 18.0, 4.0 Hz, 1H), 2.21 (br. d, *J* = 12.0 Hz, 1H), 1.90–1.97 (m, 3H), 1.50–1.61 (m, 2H), 1.43 (s, 9H), 1.05 (q, *J* = 12.0 Hz, 1H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.82 (q, *J* = 13.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.0, 154.5, 103.3, 80.0, 64.8, 64.4, 58.4, 54.7, 41.9, 40.6, 40.3, 38.8, 37.3, 31.9, 30.4, 28.4; IR (neat) ν_{max} 2914, 1709, 1691, 1396, 11366, 1151, 1170, 1120, 1043 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{31}N_1Na_1O_5]^+$: 376.2094, found : 376.2079; $[\alpha]^{27}_D$ –96 (*c* 0.6, $CHCl_3$) ; mp 79–84 °C.

Stereochemistry determination of compounds 15 – 19

Coupling constants indicated that compound **15** is *cis*-fused ring system, and compound **16** is *trans*-fused ring system.



NOEDF supported our proposed stereochemistry; see Page S57 to S62.



References

S1) Jia, Z.-J.; Zhou, Q.; Zhou, Q.-Q.; Chen, P.-Q.; Chen, Y.-C. *Angew. Chem. Int. Ed.* **2011**, *50*, 8638–8641.

S2) Kann, N.; Rein, T.; Akermark, B; Helquist, P. *J. Org. Chem*. **1990**, *55*, 5312–5323.

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S4) Li, Y.; Barløse, C.; Jørgensen, J.; Carlsen, B. D.; Jørgensen, K. A. *Chem. Eur. J.* **2017**, *23,* 38–41.

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S6) Lijun, X..; Zhubo, L.; Weipeng, D.; Jinyu, S.; Maozhong, M.; Jianfeng, X.; Hongjun, R. *Org. Biomol. Chem.* **2015***, 13*, 6333-6337.

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OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
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ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.95 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	-0.10 Hz
RGAIN	30

3

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EXMOD	single_pulse_dec
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OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	60
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.07 usec
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CTEMP	21.7 c
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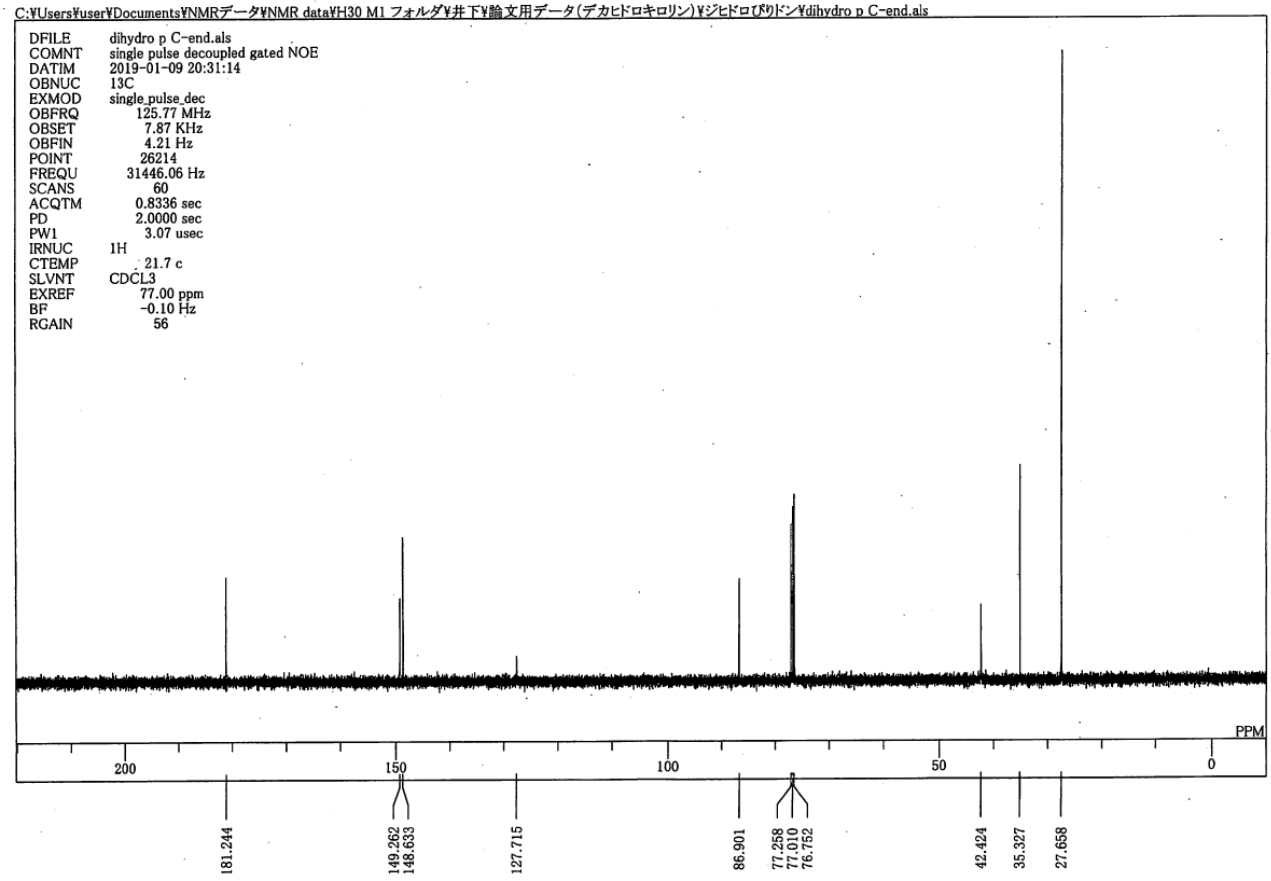
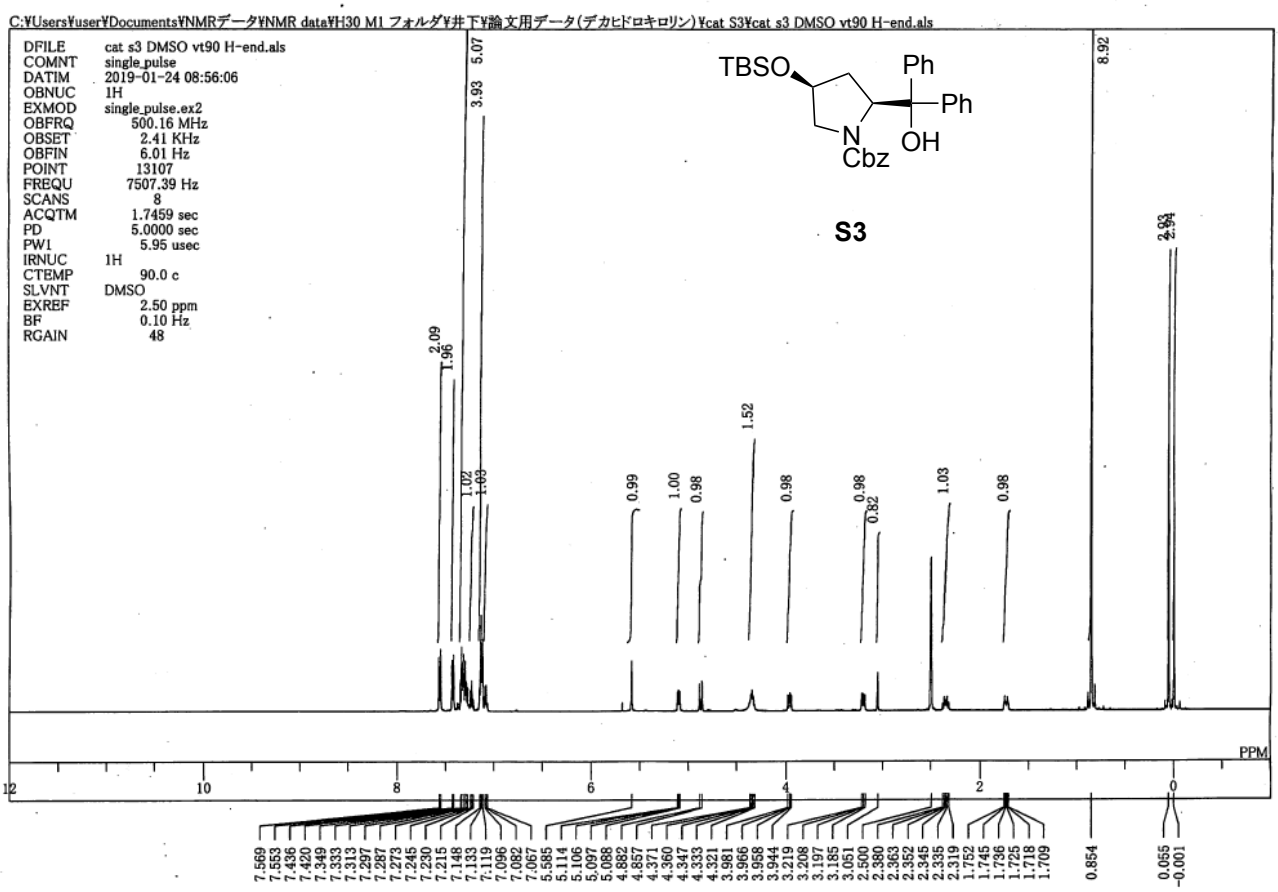
RGAIN	56

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EXMOD single_pulse.ex2
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OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 90.0 c
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EXREF 2.50 ppm
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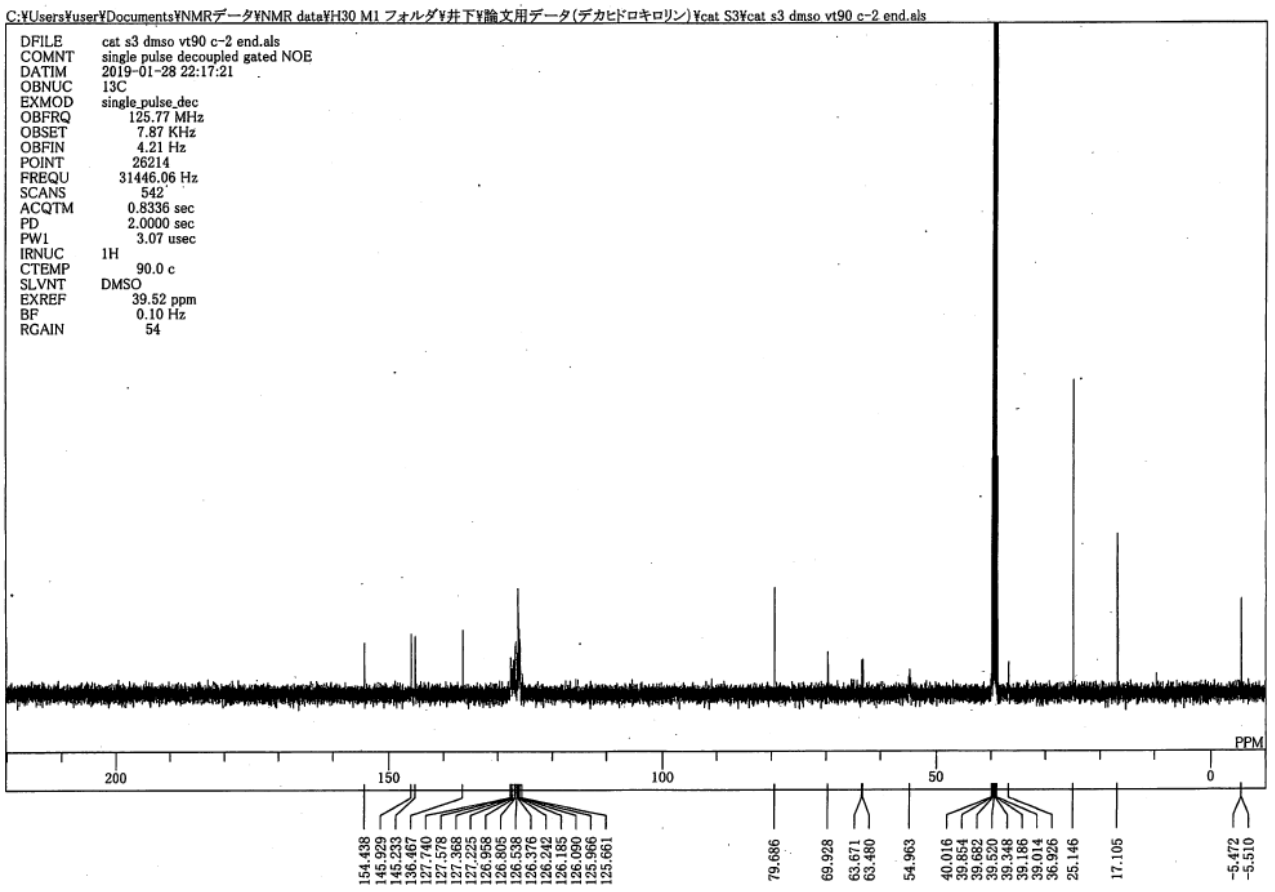
Ph
OH
N
Cbz
S3
PPM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EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 542
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 90.0 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.10 Hz
RGAIN 54
PPM

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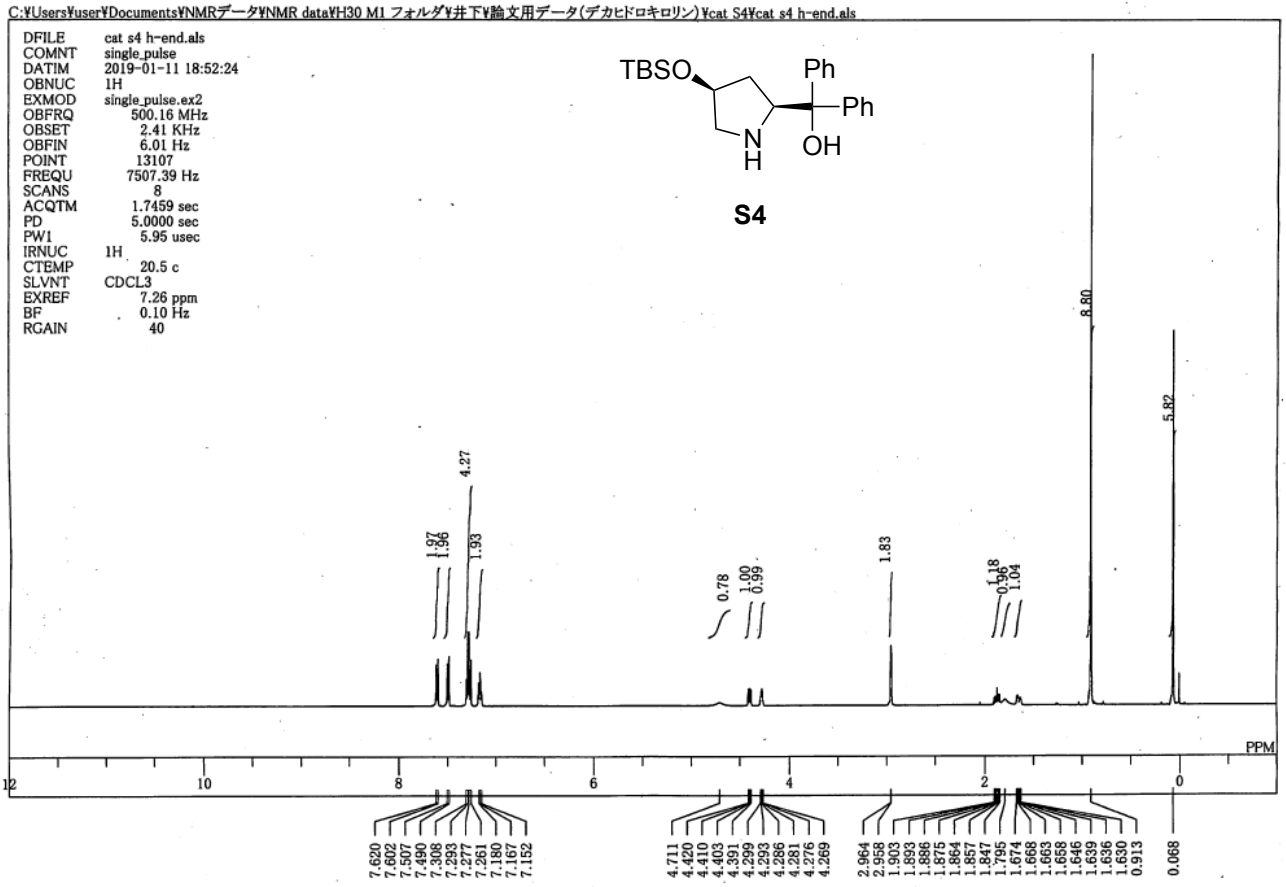

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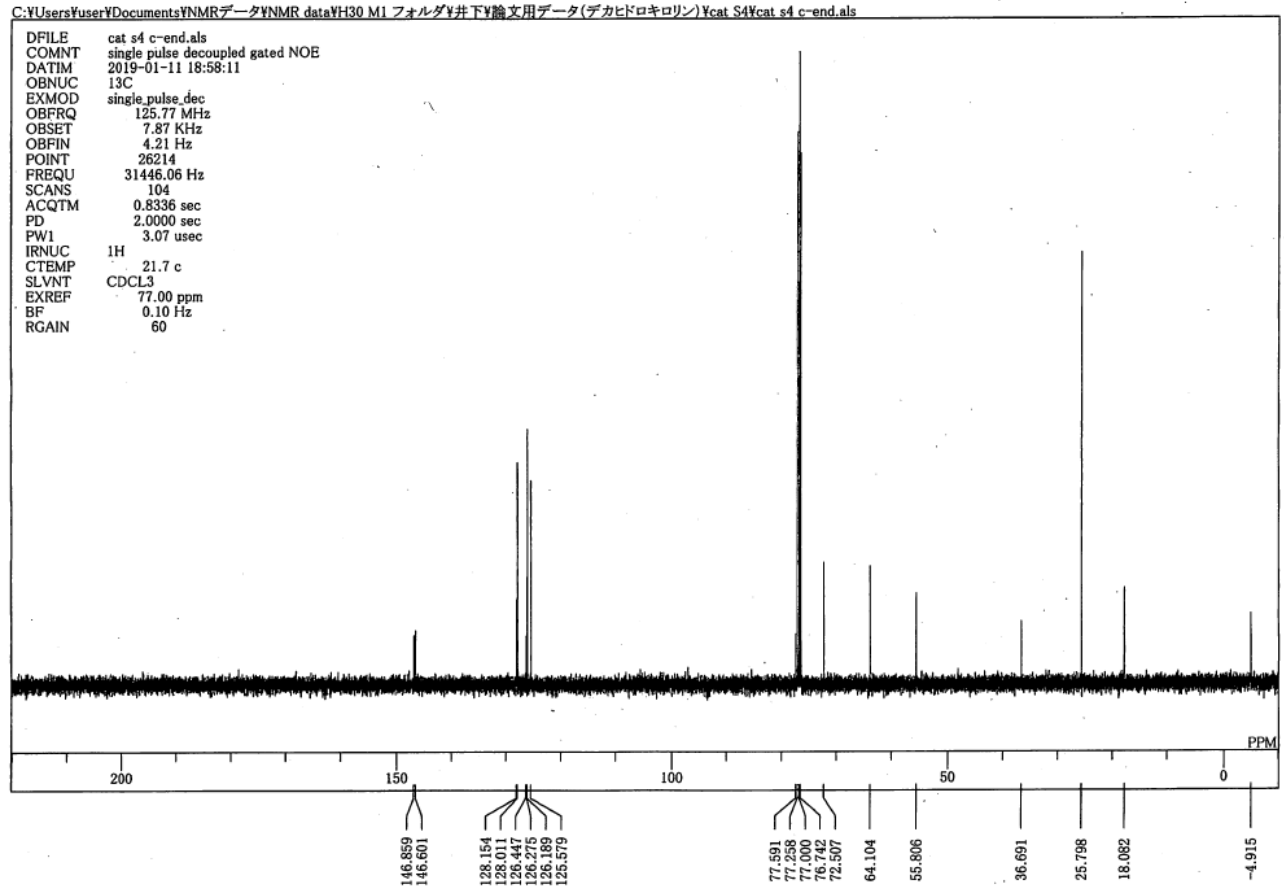

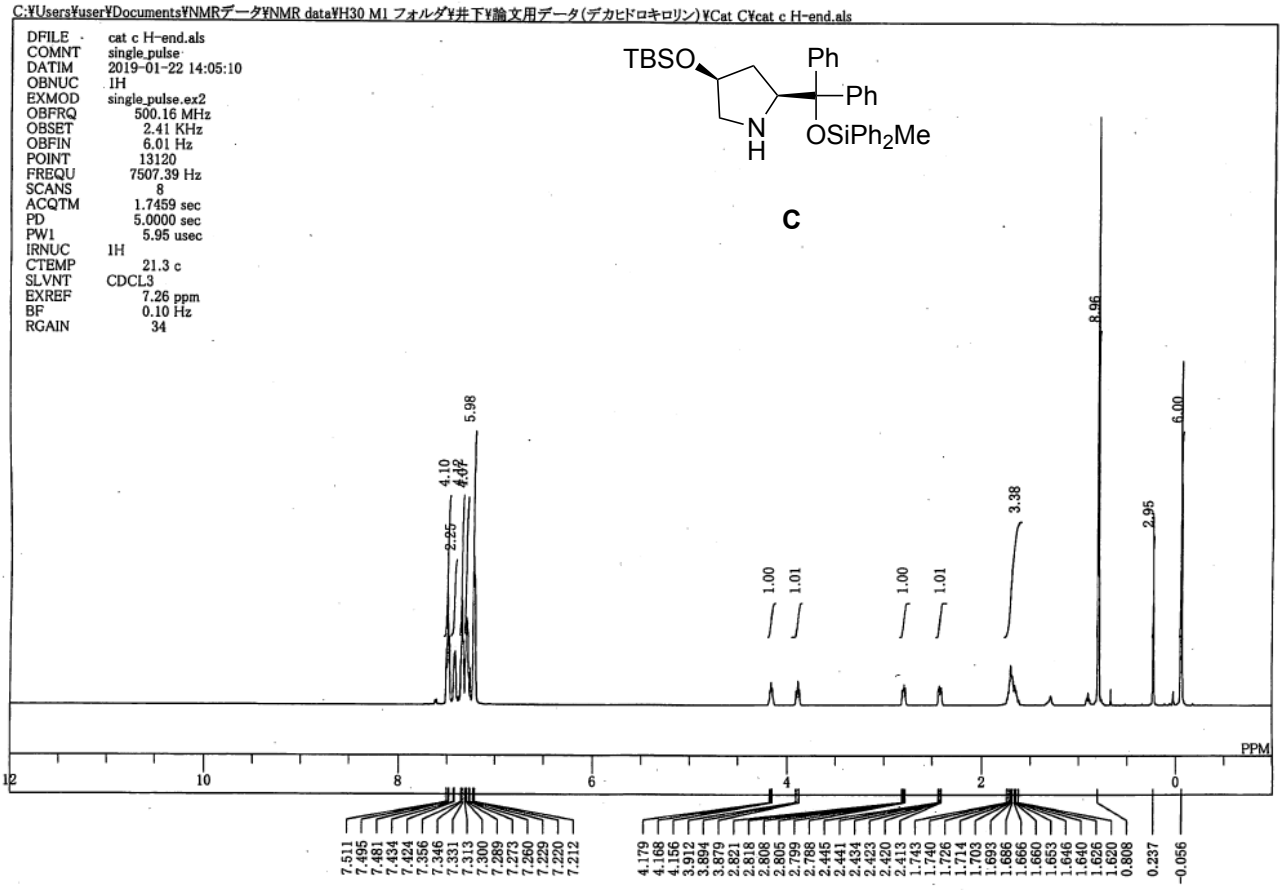
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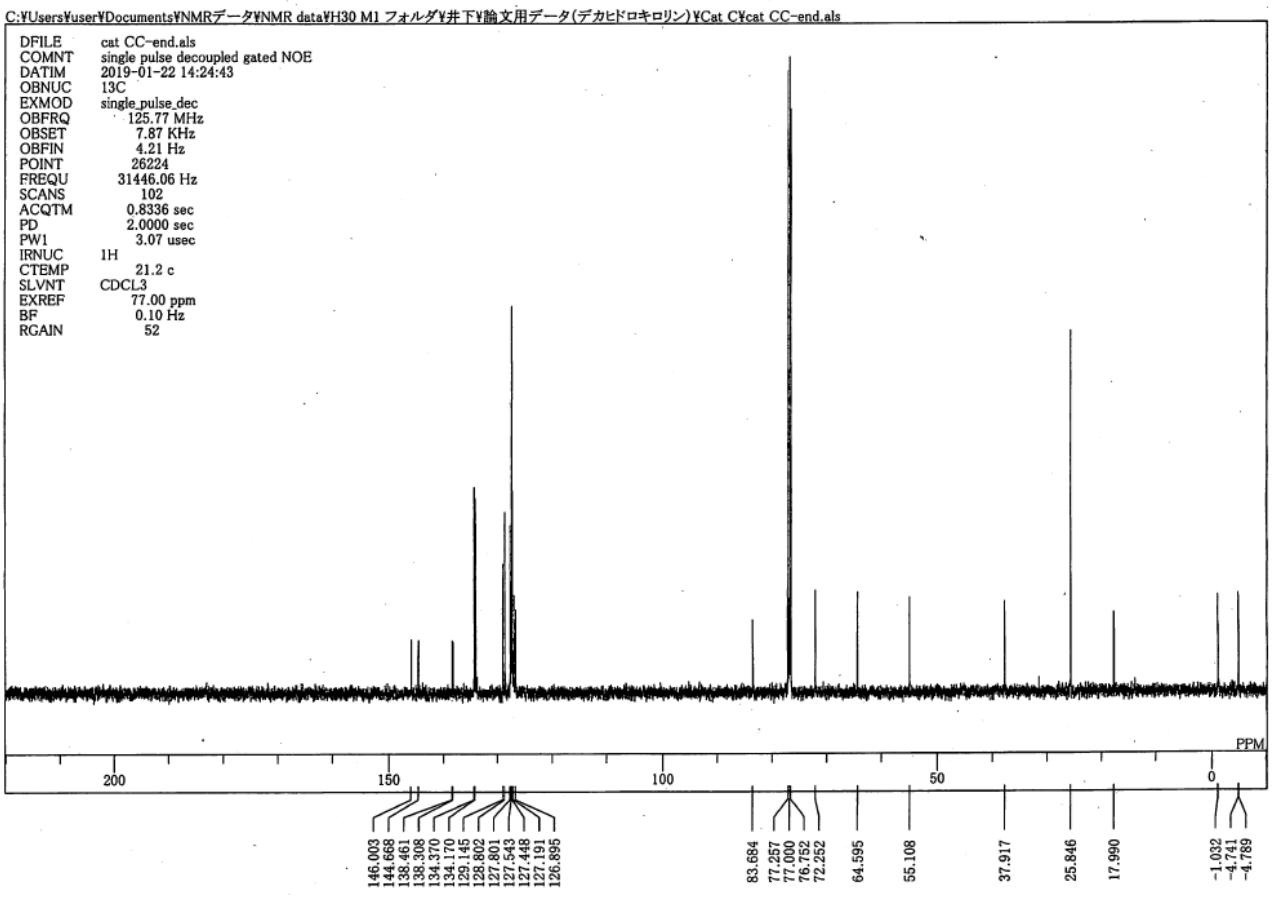
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13120
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 34
TBSO
Ph
Ph
N
H
OSiPh2Me
C
PPM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DATIM 2019-01-22 14:24:43
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26224
FREQU 31446.06 Hz
SCANS 102
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 52
PPM

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥major¥goshi major dmso VT80 hnmr-end.als

DFILE goshi major dmso VT80 hnmr-end.als
COMNT single_pulse
DATIM 2015-06-17 19:10:50
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 9384.38 Hz
SCANS 16
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.25 usec
IRNUC 1H
CTEMP 80.0 c
SLVNT DMSO
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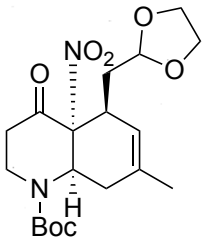
BF 0.12 Hz
RGAIN 40



4

4.805 4.706 4.686 4.670 4.244 4.236 4.227 3.393 3.289 3.279 3.264 3.256 3.240 3.231 3.188 3.177 3.163 3.153 3.139 3.128 2.892 2.863 2.836 2.500 2.469 2.366 2.349 2.311 2.294 2.278 2.262 2.243 1.962 1.953 1.943 1.930 1.919 1.903 1.780 1.765 1.743 1.728 1.682 1.661 1.626 1.618 1.606 1.598 1.588 1.576 1.569 1.042 1.010 1.001 0.981 0.971 0.870 0.843 0.797

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DFILE goshi hmqc cnmr kai-end.als
COMNT single pulse decoupled gated NOE
DATIM 2015-06-22 11:34:51
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EXMOD single_pulse_dec
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OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26224
FREQU 31446.06 Hz
SCANS 300
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
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SLVNT DMSO
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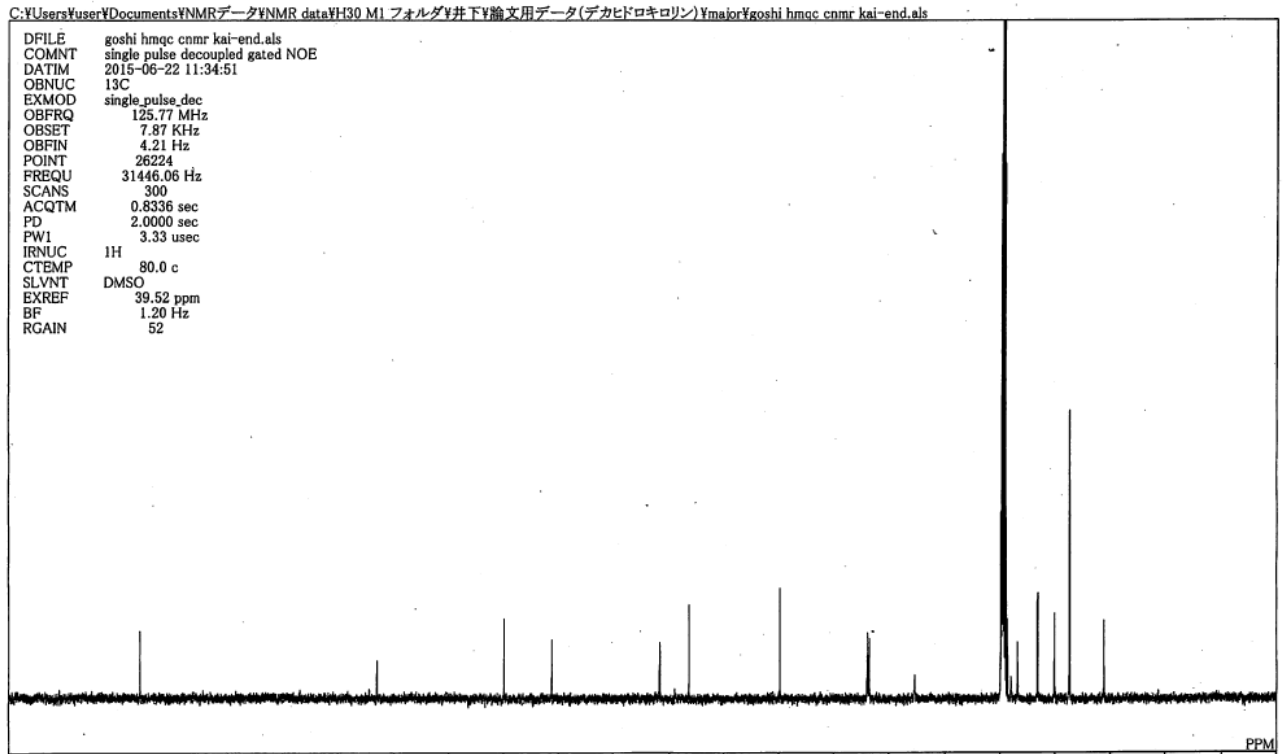
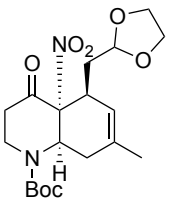
BF 1.20 Hz
RGAIN 52



196.013 153.059 129.995 121.375 101.781 96.490 79.995 64.167 63.881 55.634 40.016 39.854 39.682 39.520 39.348 39.186 39.015 38.786 38.118 36.927 33.342 30.252 27.544 21.414

=== Shimadzu LabSolutions Report ===



4

Sample Name	: CBA79 major		
Sample ID	: umeda		
Data Filename	: CBA 79 major.lcd		
Method Filename	: 10%iPrOH-Hex-floe0.5.lcm		
Batch Filename	:		
Vial#	: 1-1	Sample Type	: –¢'m
Injection Volume	: 2000 uL		
Date Acquired	: 2016/12/08 13:45:26 Acquired by	: System Administrator	
Date Processed	: 2019/03/13 21:23:02 Processed by	: System Administrator	

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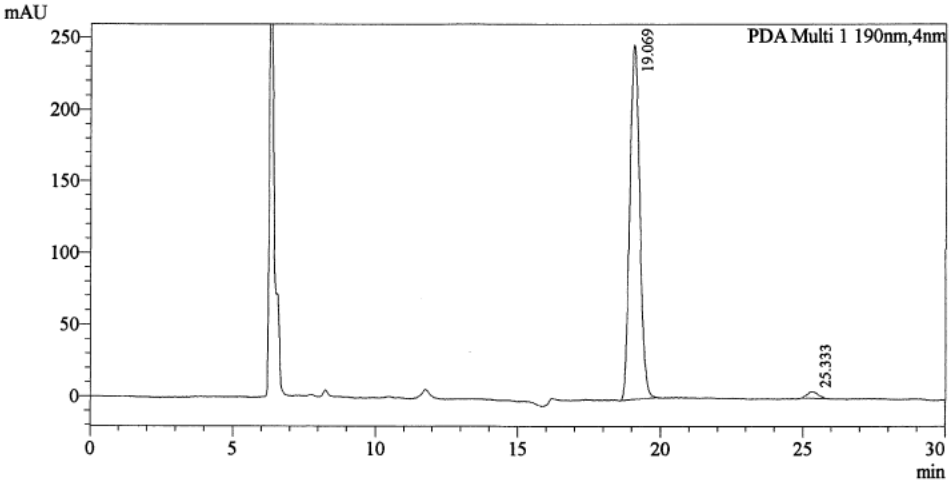

<Peak Table>

PDA Ch1 190nm

Peak#	Ret. Time	Area	Height	Conc.	Name
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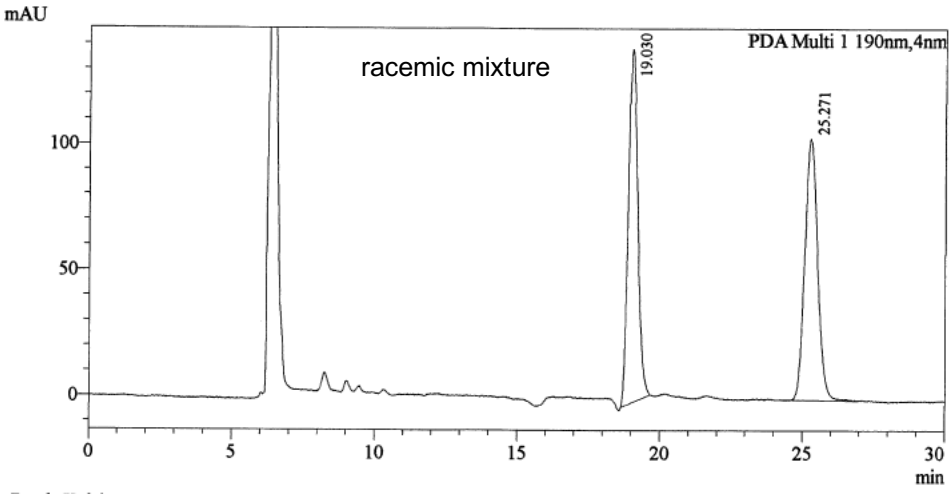

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OBNUC 1H
EXMOD single_pulse.ex2
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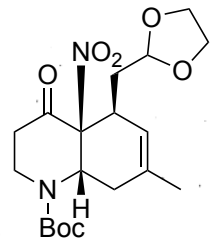
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.10 Hz
RGAIN 46



5

7.160 5.640 5.623 5.606 5.501 4.838 4.826 4.818 4.814 4.027 3.768 3.758 3.746 3.738 3.728 3.450 3.439 3.423 3.416 3.399 3.392 3.326 3.317 3.295 3.280 3.272 2.900 2.894 2.871 2.853 2.841 2.358 2.338 2.331 2.323 2.314 2.307 2.291 2.104 2.090 2.067 2.054 1.949 1.943 1.935 1.918 1.912 1.904 1.758 1.751 1.731 1.724 1.712 1.703 1.686 1.675 1.663 1.655 1.650 1.637 1.628 1.482 1.305 0.879

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DFILE Minor C-end.als
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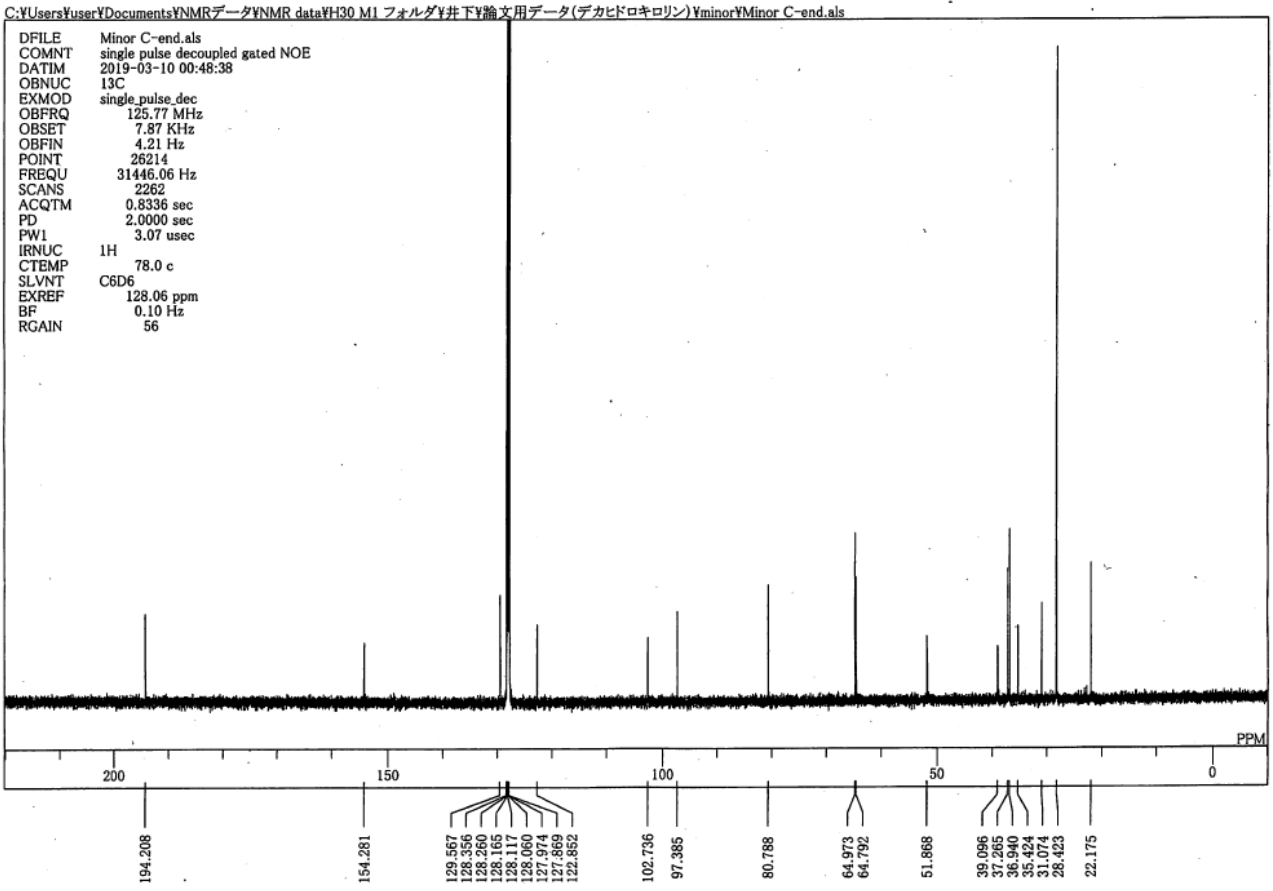
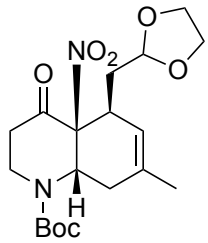
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 2262
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 128.06 ppm
BF 0.10 Hz
RGAIN 56



194.208 154.281 129.567 128.356 128.260 128.165 128.117 128.060 127.974 127.869 122.852 102.736 97.385 80.788 64.973 64.792 51.868 39.096 37.265 36.940 35.424 31.074 28.423 22.175

=== Shimadzu LabSolutions Report ===



5

Sample Name	: CBA79 minor 15mol%				
Sample ID	: umeda				
Data Filename	: CBA79 minor 15mol%.lcd				
Method Filename	: 10%iPrOH-Hex-flow0.5.lcm				
Batch Filename	:				
Vial#	: 1-1		Sample Type	: –¢'m	
Injection Volume	: 2000 uL				
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Date Processed	: 2016/12/13 17:02:24	Processed by	: System Administrator		

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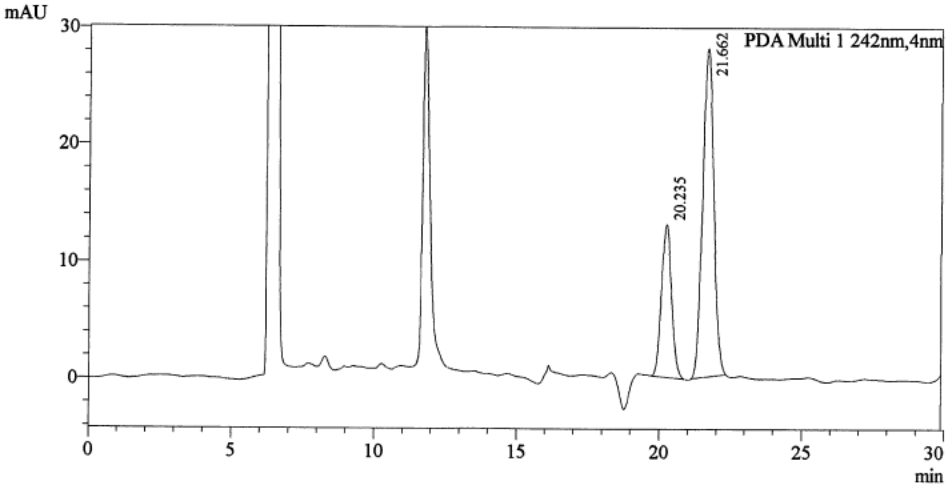

<Peak Table>

PDA Ch1 242nm

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‡Œv		1077325	41196		

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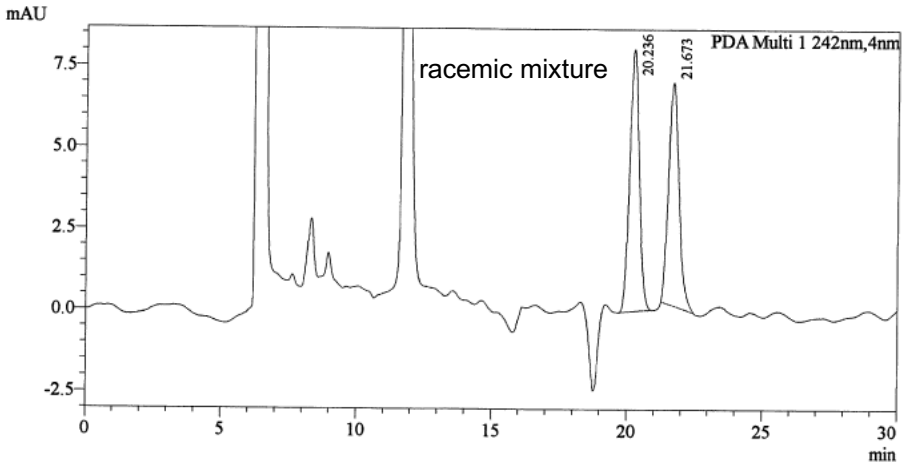
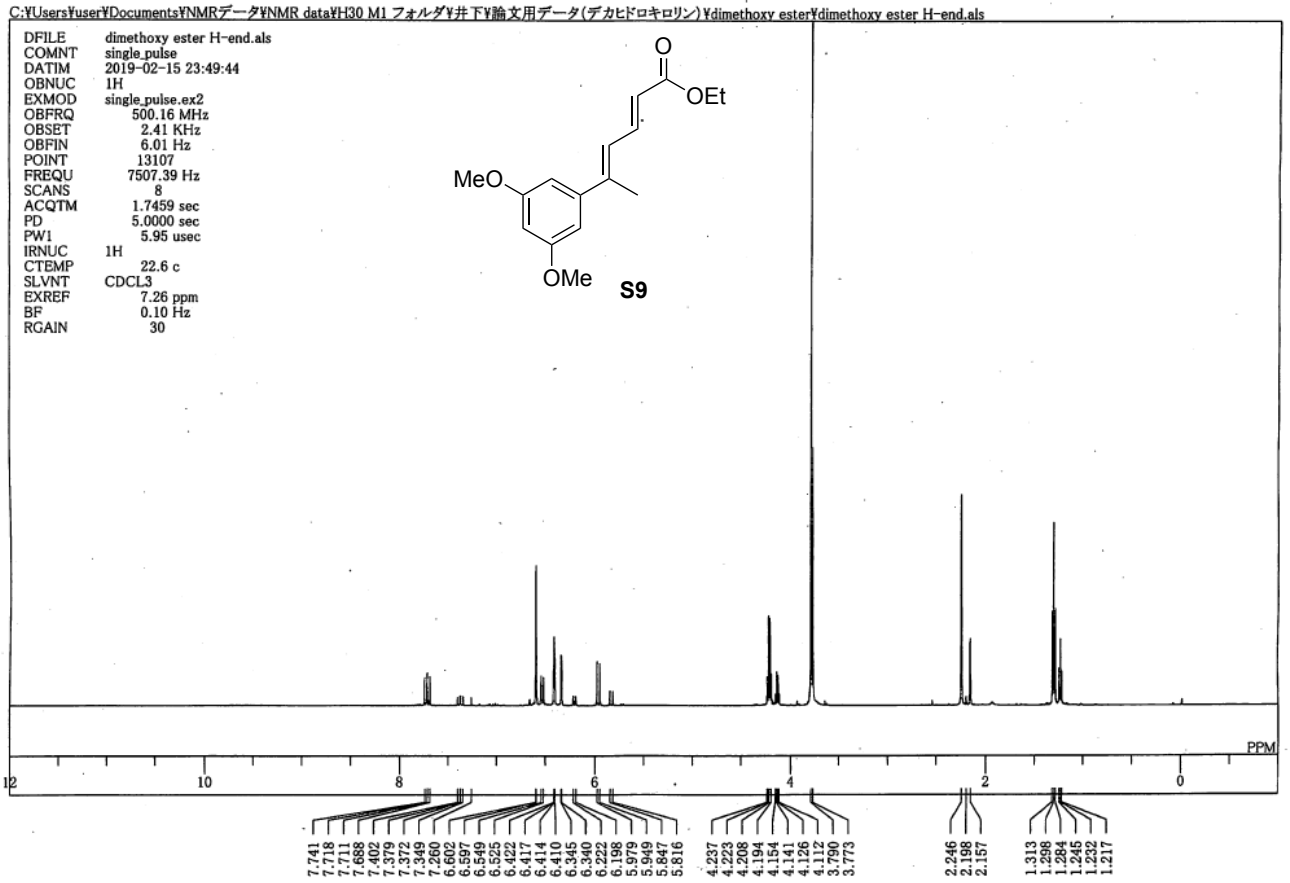
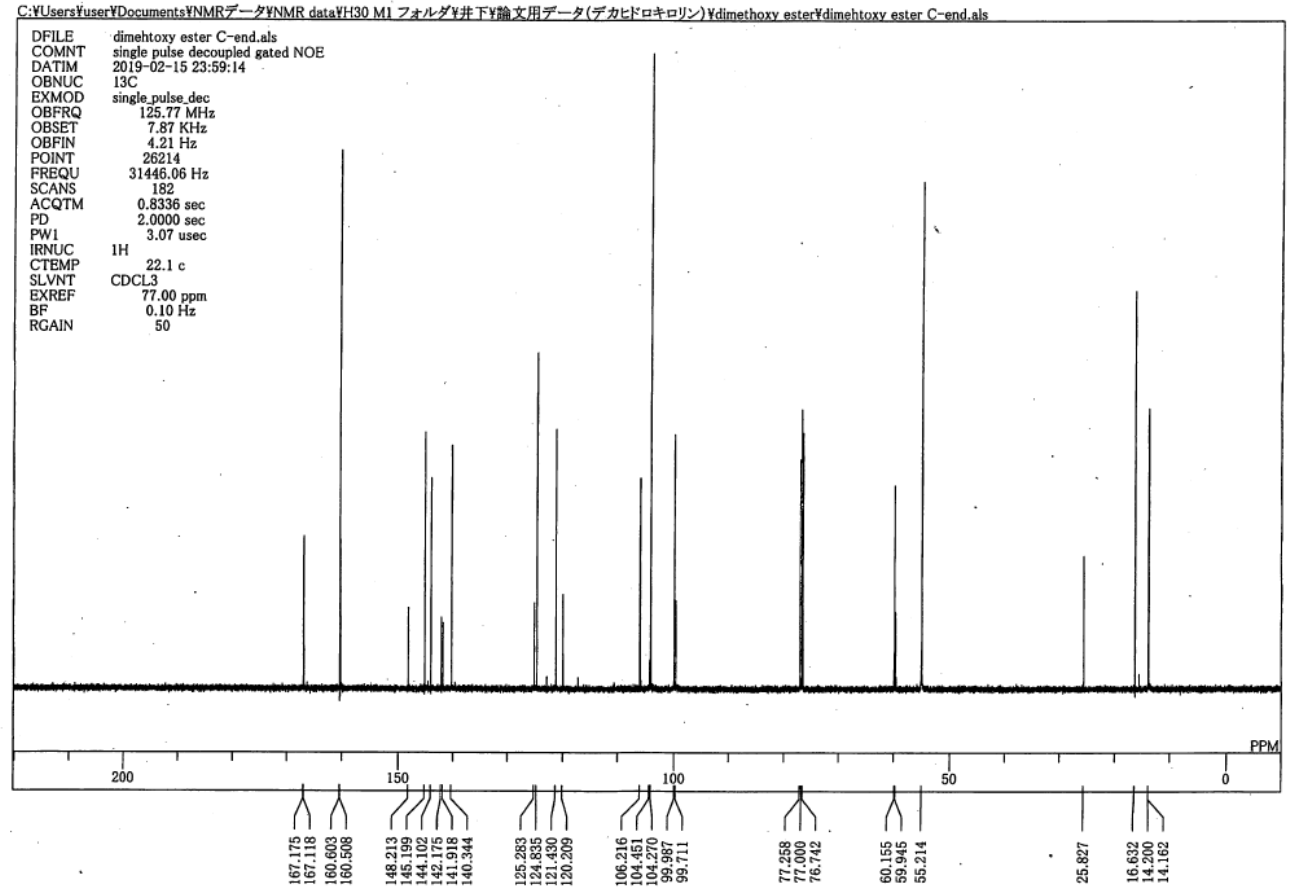


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥dimethoxy ester¥dimethoxy ester H-end.als



S9

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥dimethoxy ester¥dimehtoxy ester C-end.als



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥ニトロアルコール¥nitro alcohol H-end.als

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DATIM 2018-12-25 15:27:30
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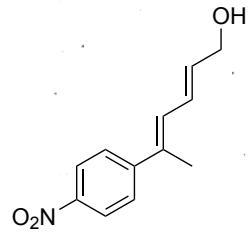
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 7.26 ppm
BF -0.10 Hz
RGAIN 36



S5

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥ニトロアルコール¥nitro alcohol C-end.als

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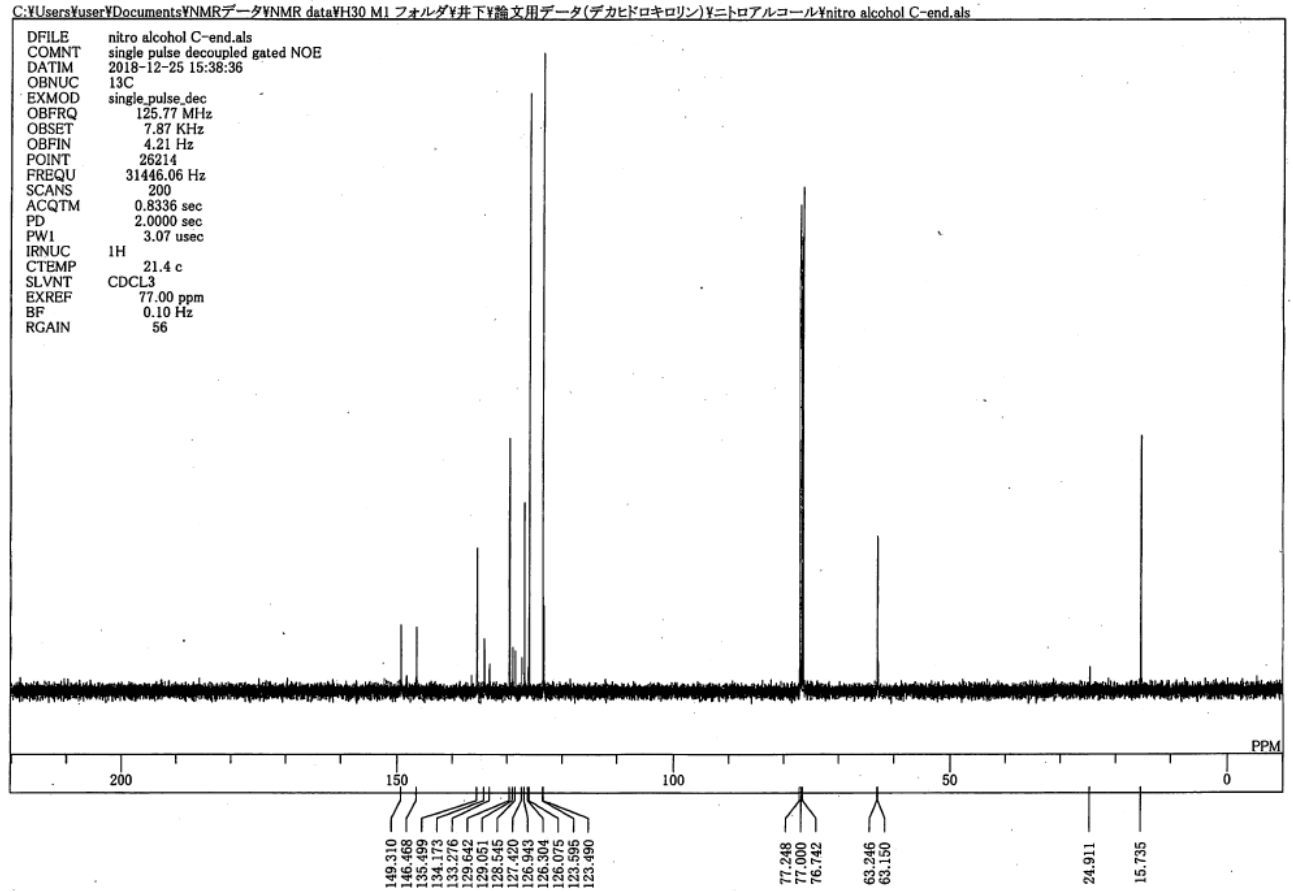
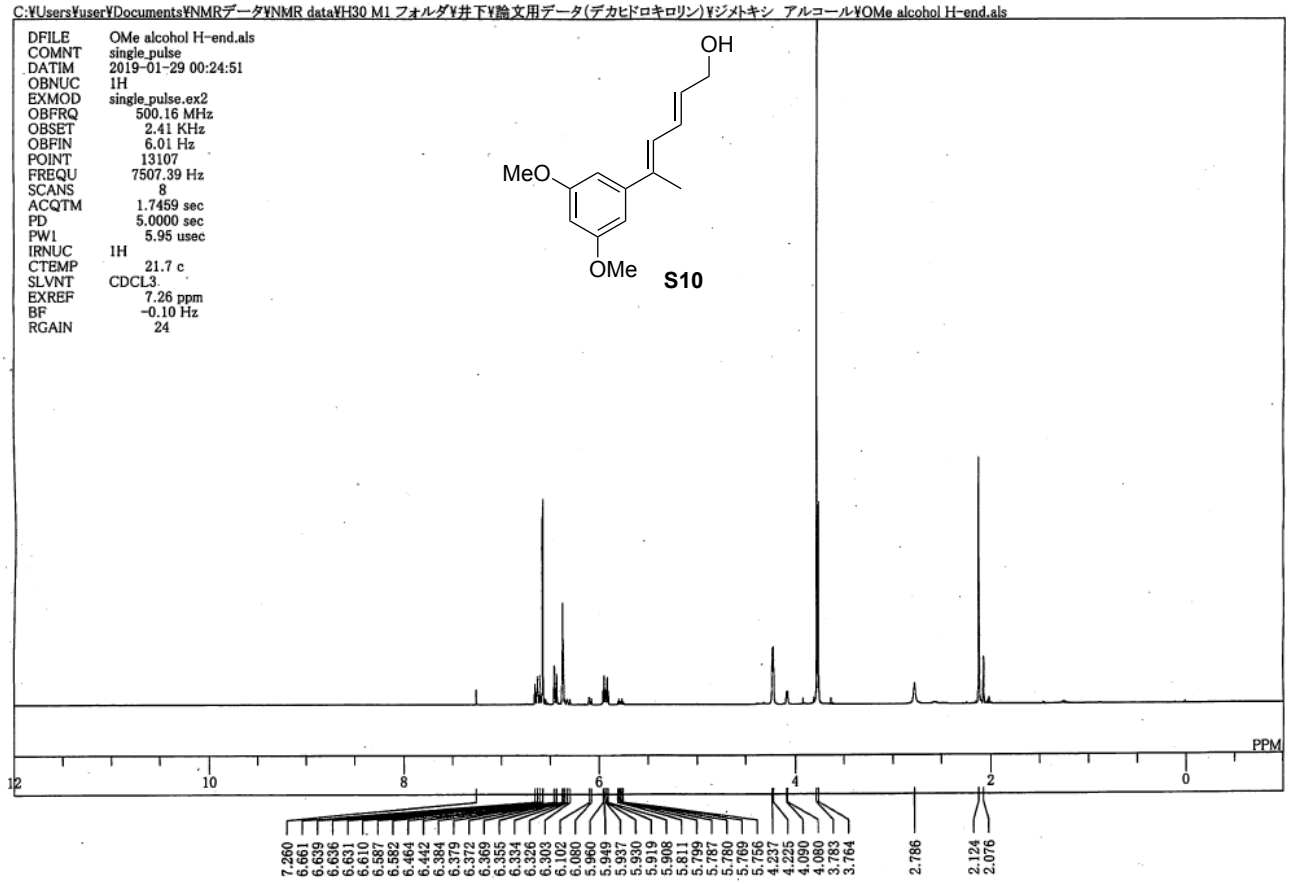
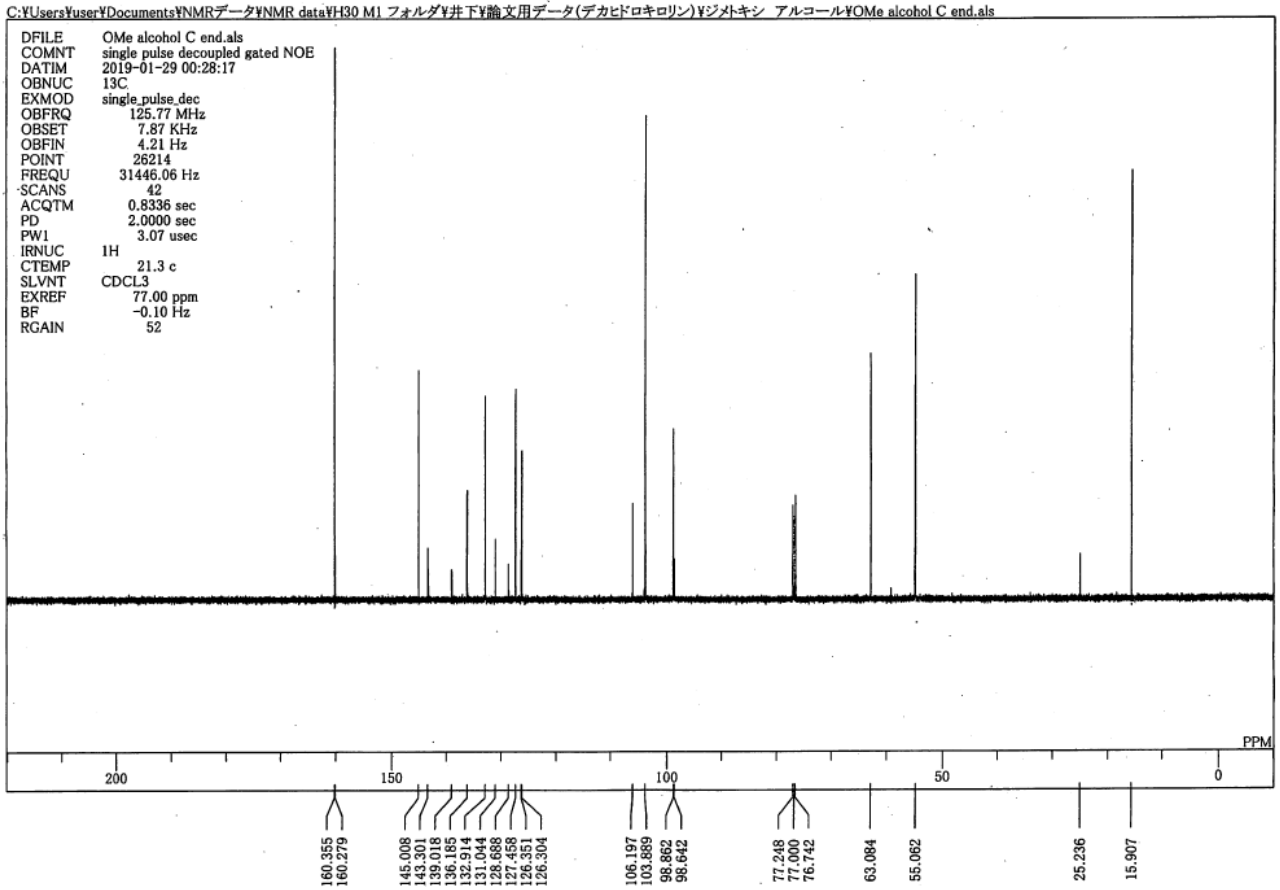
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 200
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 56



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥ジメトキシ アルコール¥OMe alcohol H-end.als

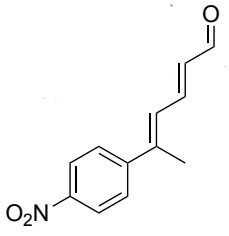


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥ジメトキシ アルコール¥OMe alcohol C end.als

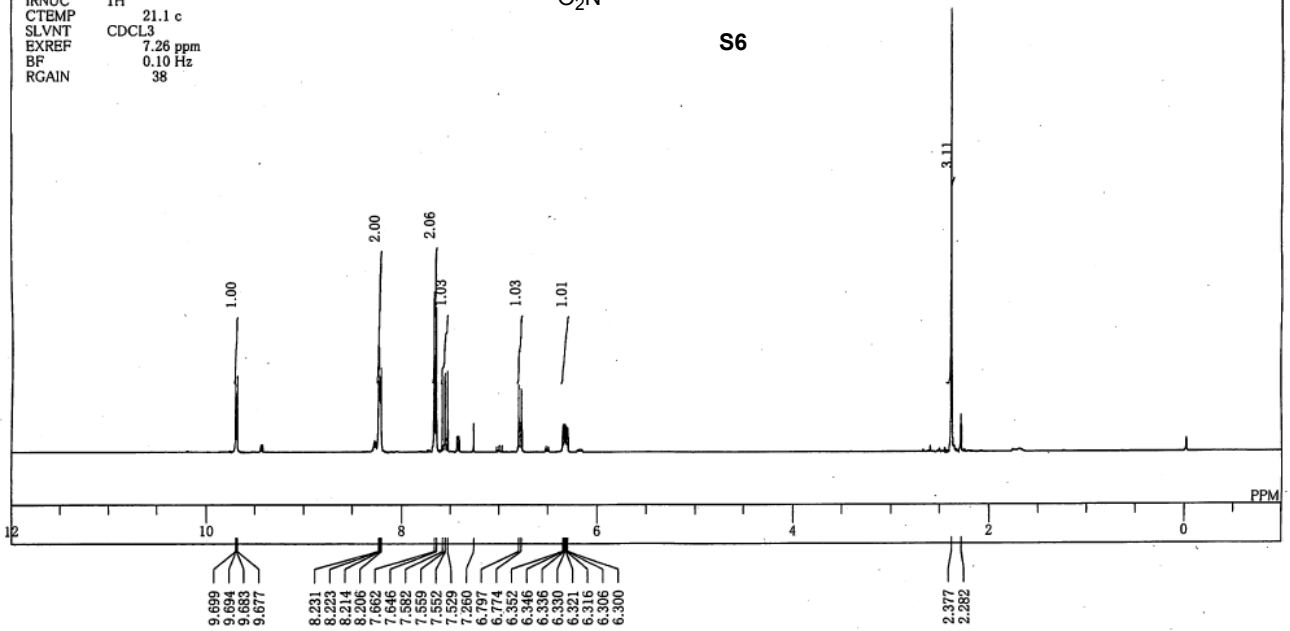


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥ニトロアルデヒド¥nitro aldehyde H-end.als

DFILE nitro aldehyde H-end.als
COMNT single_pulse
DATIM 2018-12-21 13:17:23
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 38



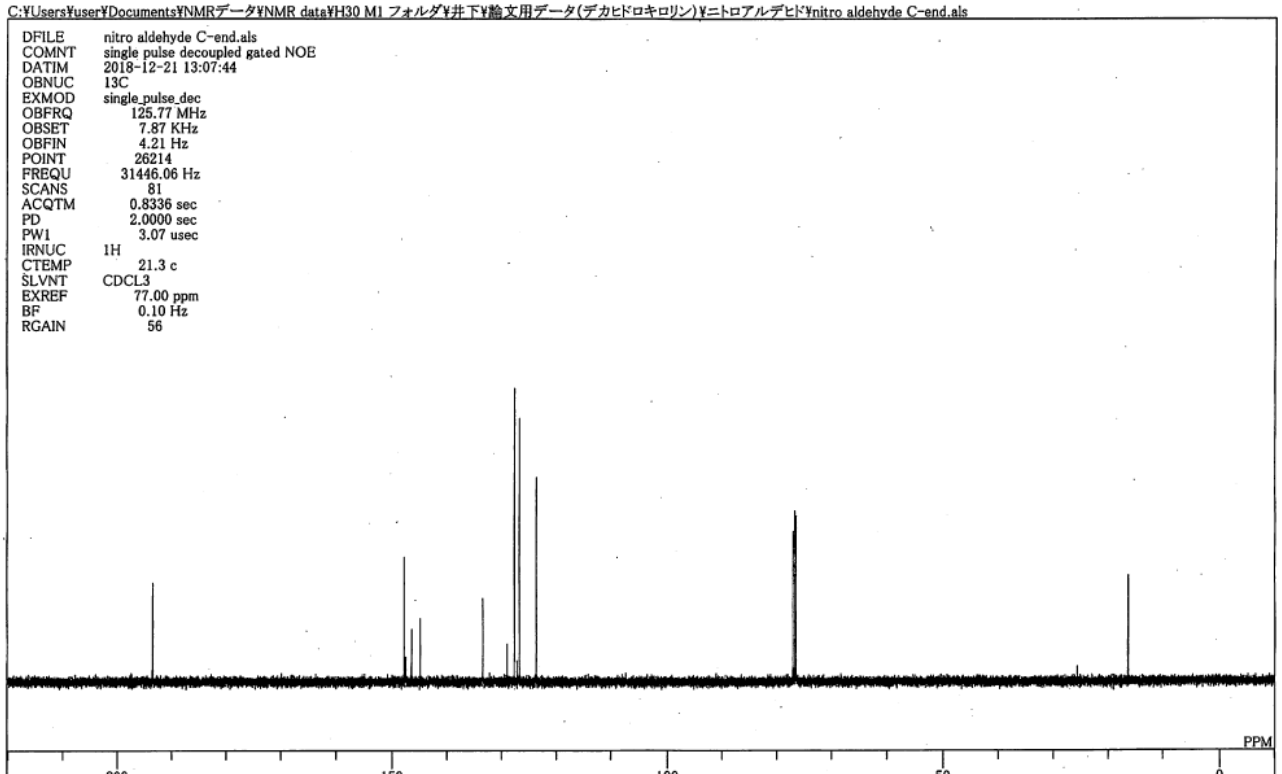
S6



9.699 9.694 9.683 9.677 8.231 8.223 8.214 8.206 7.662 7.646 7.582 7.559 7.552 7.529 7.260 6.797 6.774 6.352 6.346 6.336 6.330 6.321 6.316 6.306 6.300 2.377 2.282

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥ニトロアルデヒド¥nitro aldehyde C-end.als

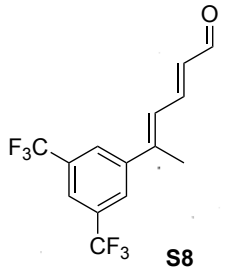
DFILE nitro aldehyde C-end.als
COMNT single pulse decoupled gated NOE
DATIM 2018-12-21 13:07:44
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 81
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 56



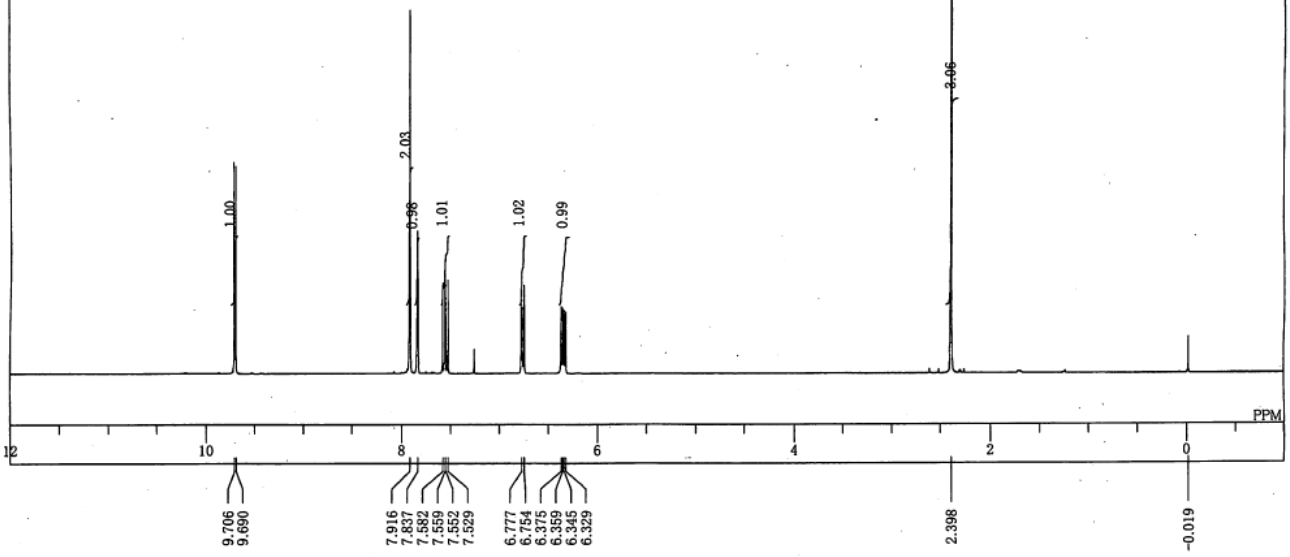
193.444 147.774 146.391 144.856 133.495 129.012 127.706 126.857 123.785 77.248 77.000 76.742 16.670

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥トリフルオロ アルデヒド¥CF3 aldehyde H-end.als

DFILE CF3 aldehyde H-end.als
COMNT single_pulse
DATIM 2018-12-25 09:36:26
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 36



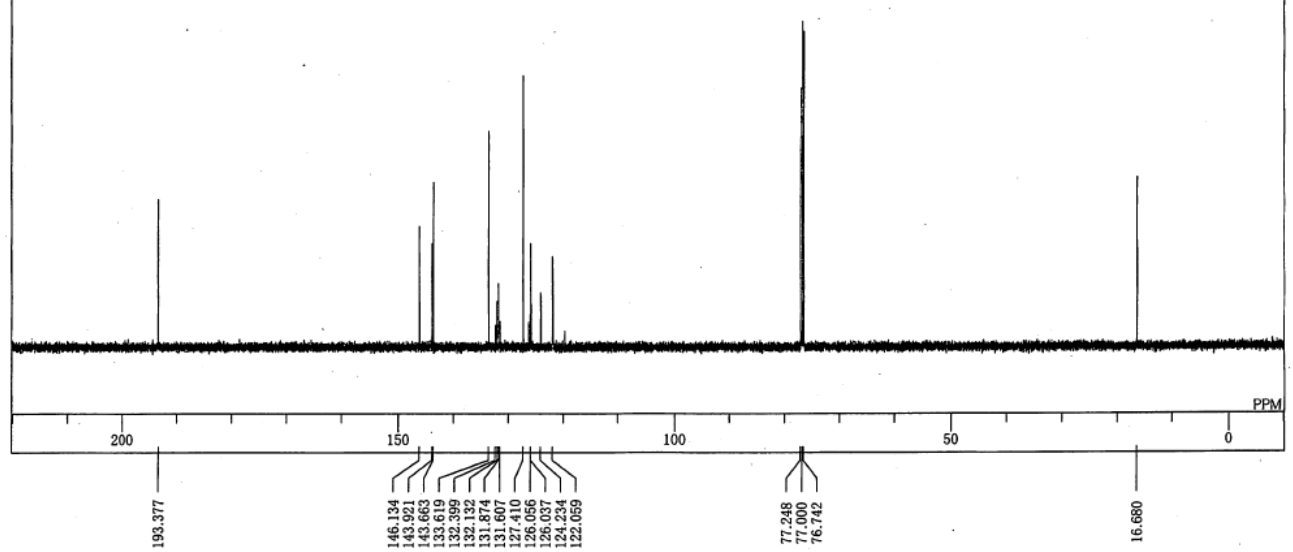
S8



9.706, 9.690, 7.916, 7.837, 7.582, 7.559, 7.552, 7.529, 6.777, 6.754, 6.375, 6.359, 6.345, 6.329, 2.398, −0.019

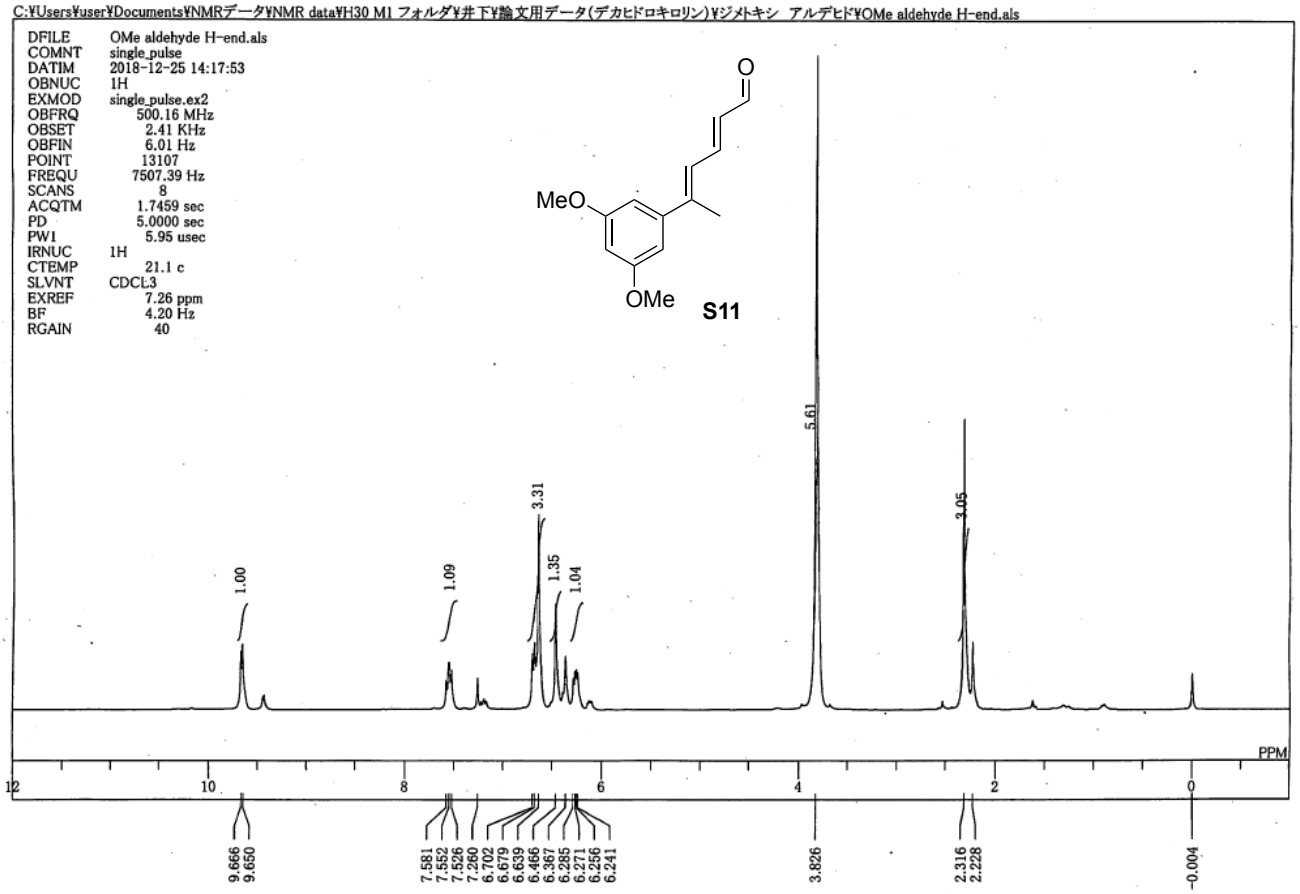
C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥トリフルオロ アルデヒド¥CF3 aldehyde C-end.als

DFILE CF3 aldehyde C-end.als
COMNT single pulse decoupled gated NOE
DATIM 2018-12-25 09:43:35
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 124
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 21.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 60

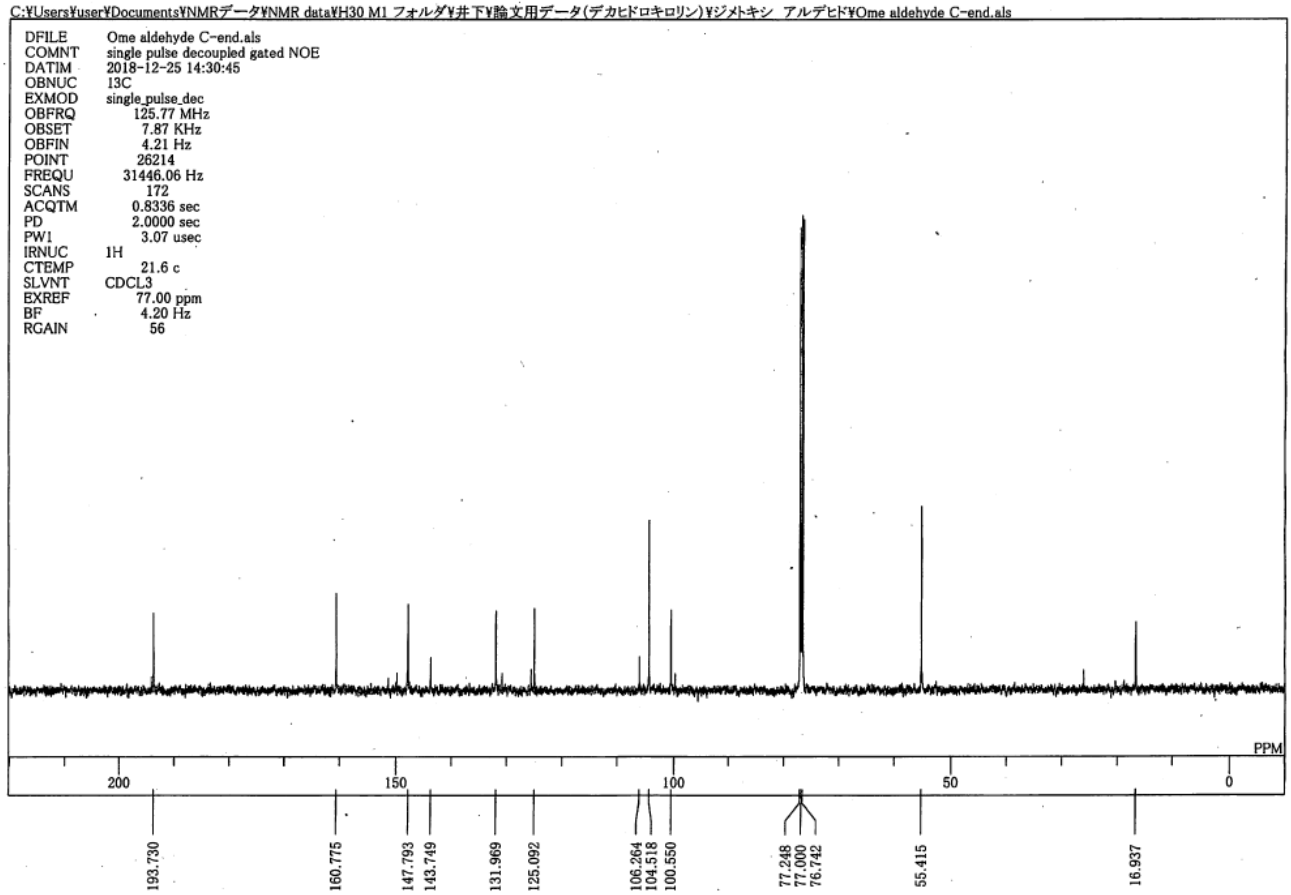


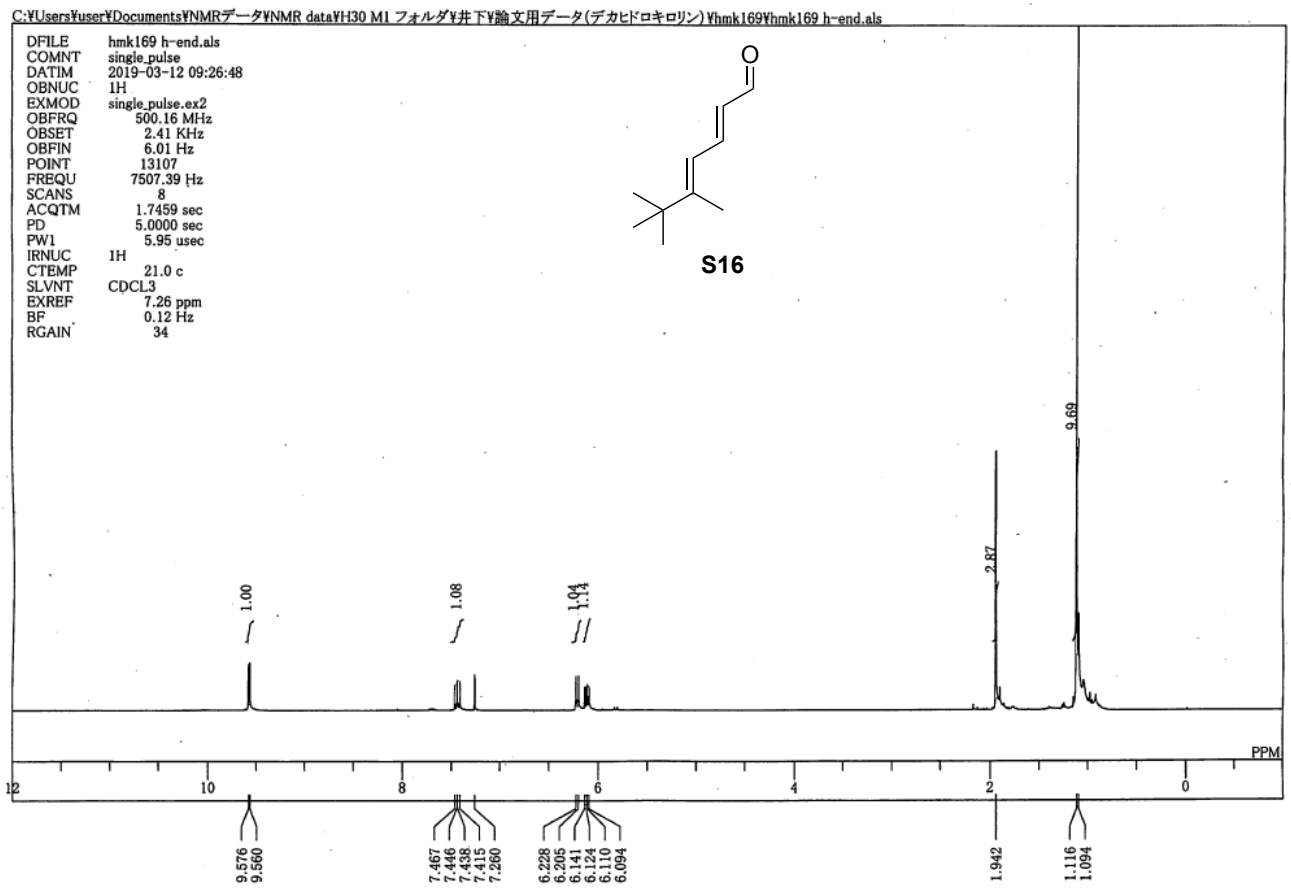
193.377, 146.134, 143.921, 143.663, 133.619, 132.399, 132.132, 131.874, 131.607, 127.410, 126.056, 126.037, 124.234, 122.059, 77.248, 77.000, 76.742, 16.680

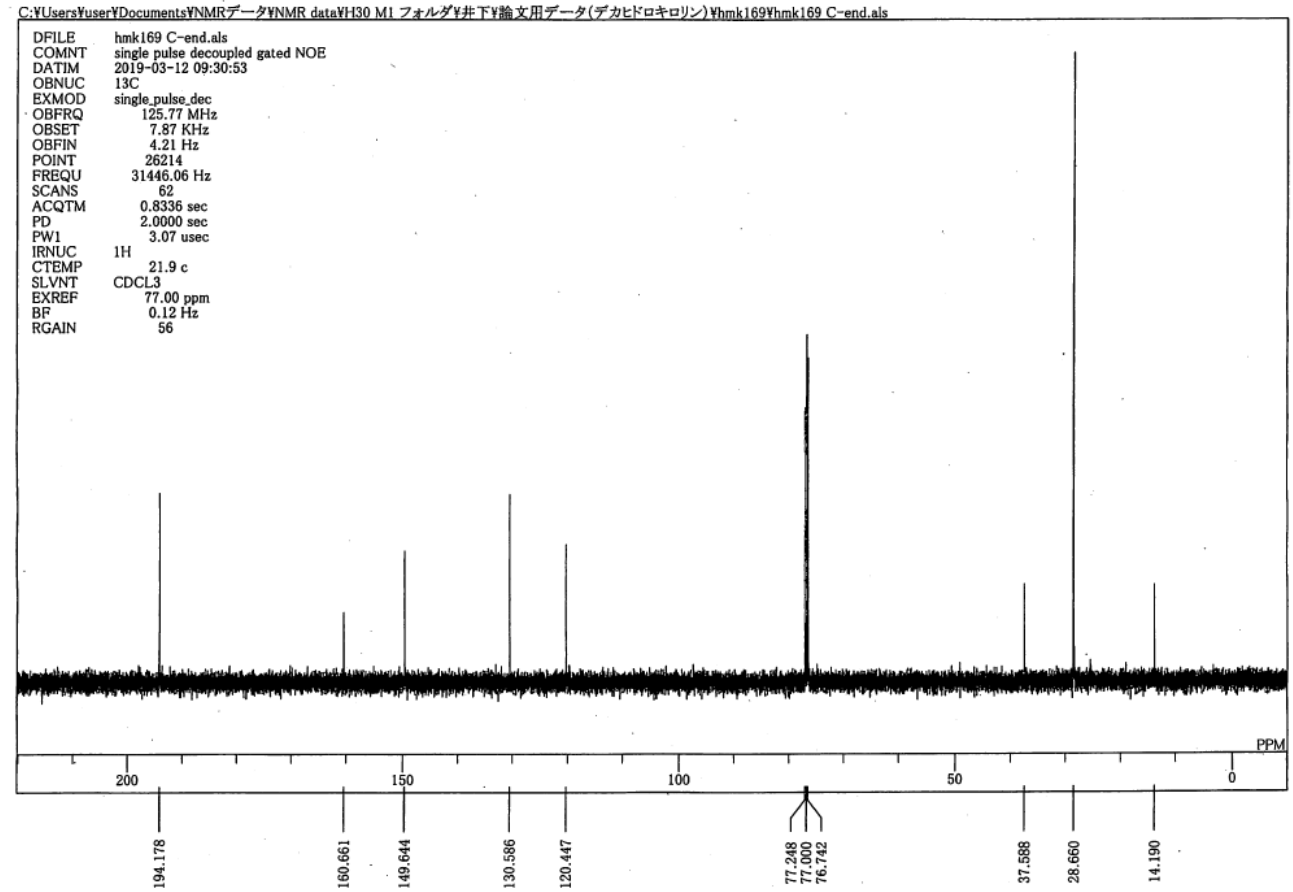
C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥ジメトキシ アルデヒド¥OMe aldehyde H-end.als



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥ジメトキシ アルデヒド¥Ome aldehyde C-end.als

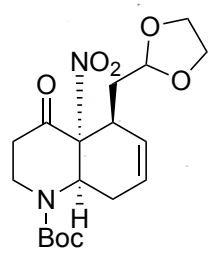



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk169¥hmk169 h-end.als
DFILE hmk169 h-end.als
COMNT single_pulse
DATIM 2019-03-12 09:26:48
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 34
O
S16
1.00
1.08
1.04
1.14
2.87
9.69
PPM
12
10
8
6
4
2
0
9.576
9.560
7.467
7.446
7.438
7.415
7.260
6.228
6.205
6.141
6.124
6.110
6.094
1.942
1.116
1.094


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk169¥hmk169 C-end.als
DFILE hmk169 C-end.als
COMNT single pulse decoupled gated NOE
DATIM 2019-03-12 09:30:53
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 62
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 56
PPM
200
150
100
50
0
194.178
160.661
149.644
130.586
120.447
77.248
77.000
76.742
37.588
28.660
14.190

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk11,12¥hmk11,12 h-end.als

DFILE	hmk11,12 h-end.als
COMNT	single_pulse
DATIM	2019-02-04 06:06:54
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.95 usec
IRNUC	1H
CTEMP	55.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	4.20 Hz
RGAIN	42

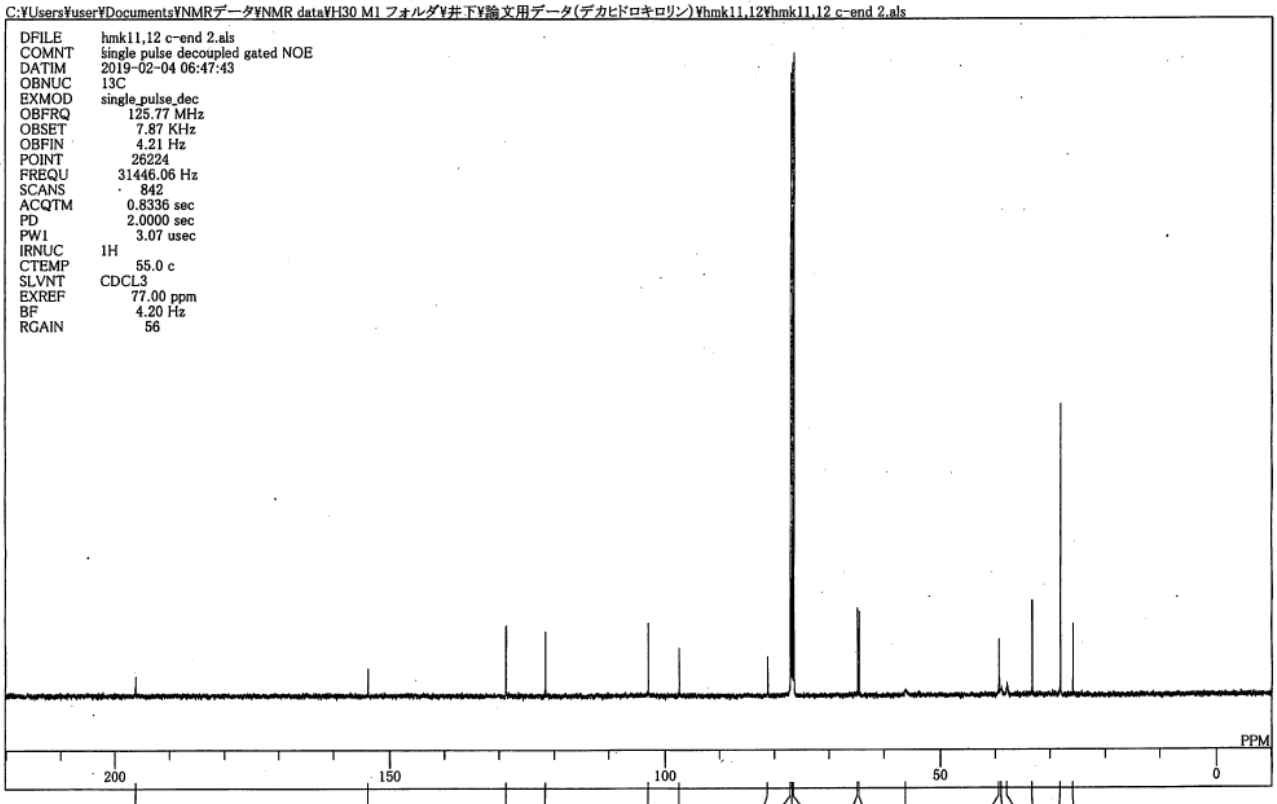


6

7.260 5.780 5.759 5.548 5.529 5.430 4.896 4.888 4.880 4.304 3.959 3.949 3.934 3.925 3.910 3.900 3.846 3.835 3.820 3.810 3.796 3.784 3.338 3.058 3.040 3.027 3.020 3.009 2.989 2.470 2.461 2.454 2.439 2.432 2.424 2.384 2.377 2.365 2.355 2.346 2.335 2.327 2.212 1.670 1.643 1.497

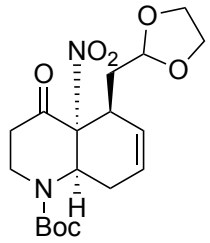
C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk11,12¥hmk11,12 c-end 2.als

DFILE	hmk11,12 c-end 2.als
COMNT	single pulse decoupled gated NOE
DATIM	2019-02-04 06:47:43
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26224
FREQU	31446.06 Hz
SCANS	842
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.07 usec
IRNUC	1H
CTEMP	55.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	4.20 Hz
RGAIN	56



196.184 153.926 128.831 121.765 103.087 97.509 81.424 77.248 77.000 76.743 65.120 64.853 56.443 39.443 39.061 37.975 33.465 28.278 26.047

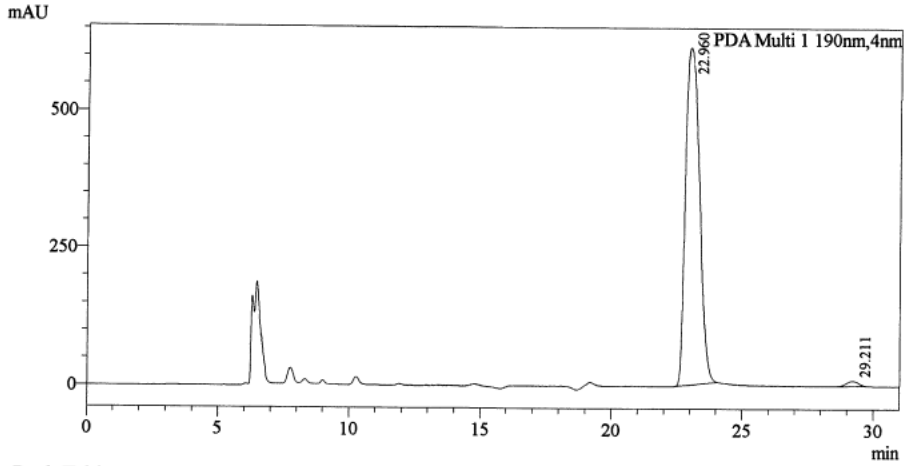
=== Shimadzu LabSolutions Report ===



6

Sample Name	: CBA87 20mol% major right``		
Sample ID	: umeda		
Data Filename	: CBA87 20mol% major right``.lcd		
Method Filename	: 10%iPrOH-Hex-flow0.5.lcm		
Batch Filename	:		
Vial#	: 1-1	Sample Type	: ¬¢'m
Injection Volume	: 2000 uL		
Date Acquired	: 2017/01/19 16:03:36 Acquired by	: System Administrator	
Date Processed	: 2017/01/19 16:43:40 Processed by	: System Administrator	

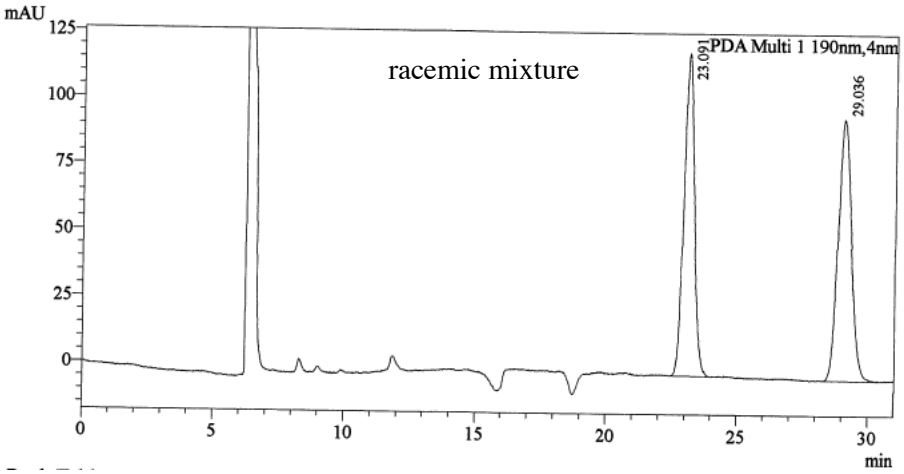
<Chromatogram>



<Peak Table>

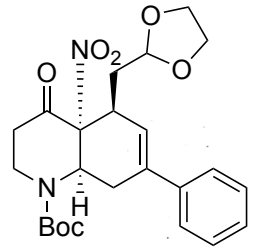
PDA Ch1 190nm

Peak#	Ret. Time	Area	Height	Conc.	Name
1	22.960	23290468	614438	98.590	
2	29.211	332999	9988	1.410	
‡Œv		23623466	624426		



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk40¥hmk40 H re -end.als

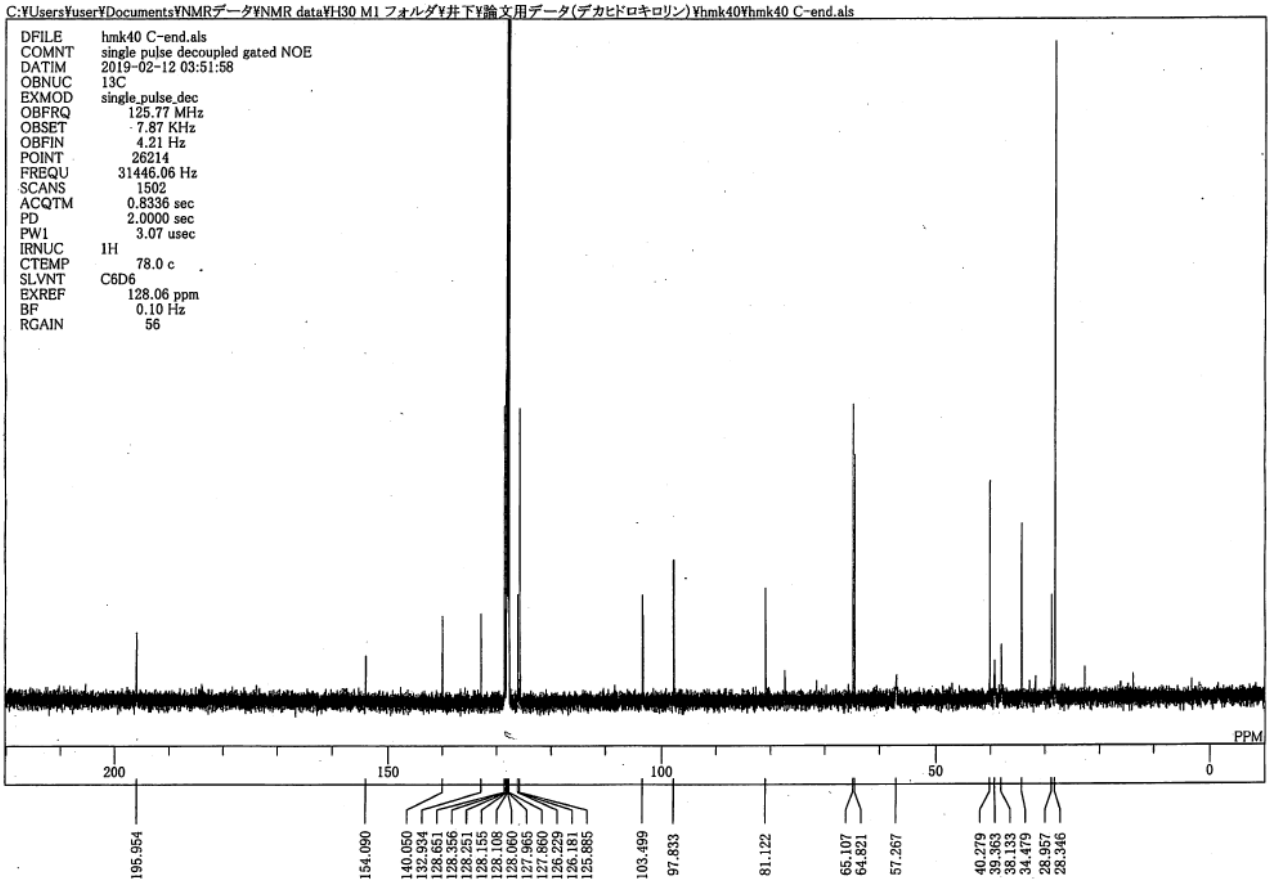
DFILE hmk40 H re -end.als
COMNT single_pulse
DATIM 2019-03-08 22:45:07
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.10 Hz
RGAIN 56

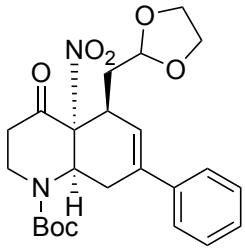


7

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk40¥hmk40 C-end.als

DFILE hmk40 C-end.als
COMNT single pulse decoupled gated NOE
DATIM 2019-02-12 03:51:58
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1502
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 128.06 ppm
BF 0.10 Hz
RGAIN 56



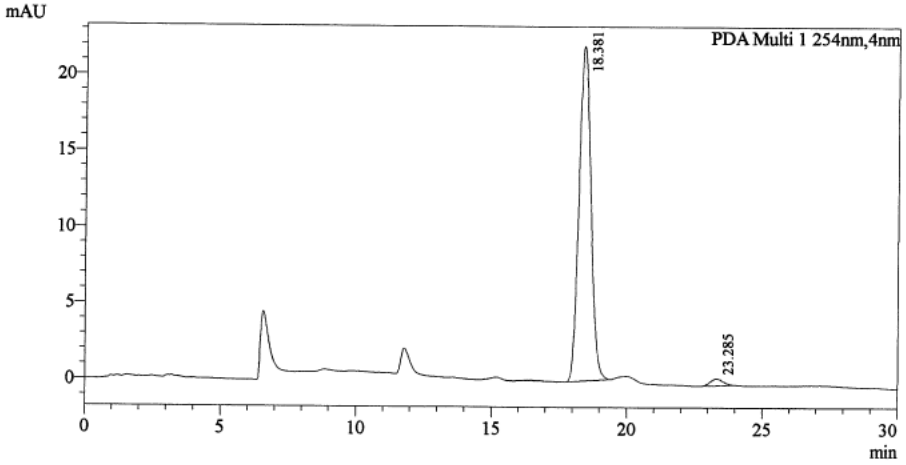


7

=== Shimadzu LabSolutions Report ===

Sample Name	: HMK30 ee fr14		
Sample ID	: inoshita		
Data Filename	: HMK30 ee fr14.lcd		
Method Filename	: 10%iPrOH-Hex-flow0.5.lcm		
Batch Filename	:		
Vial#	: 1-1	Sample Type	: –¢'m
Injection Volume	: 2000 uL		
Date Acquired	: 2017/10/30 16:39:44	Acquired by	: System Administrator
Date Processed	: 2019/03/13 20:08:39	Processed by	: System Administrator

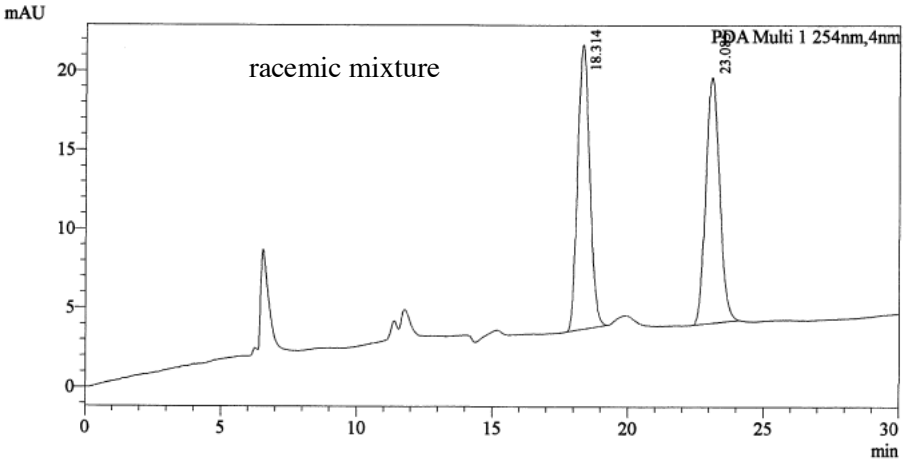
<Chromatogram>



<Peak Table>

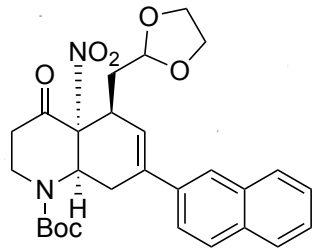
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Name
1	18.381	673004	22008	97.688	
2	23.285	15929	462	2.312	
‡Œv		688933	22470		



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk139¥hmk139 H re-end.als

DFILE hmk139 H re-end.als
COMNT single_pulse
DATIM 2019-03-08 20:30:28
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.10 Hz
RGAIN 52

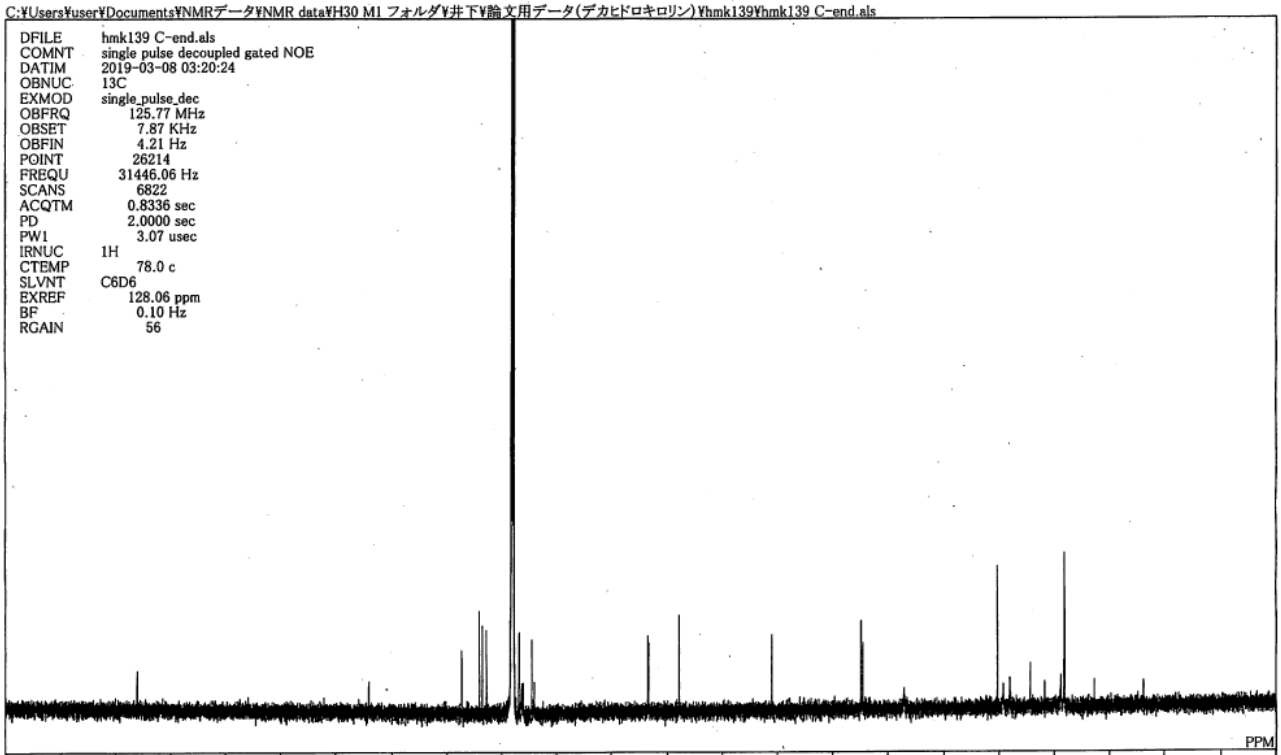


8

7.619 7.607 7.593 7.580 7.562 7.374 7.357 7.286 7.272 7.257 7.242 7.229 7.160 6.358 5.874 4.779 4.772 4.117 3.461 3.445 3.302 3.296 2.971 2.861 2.779 2.758 2.743 2.726 2.716 2.695 2.687 2.414 2.246 2.220 2.022 1.991 1.467 1.250 0.881 0.866 0.460

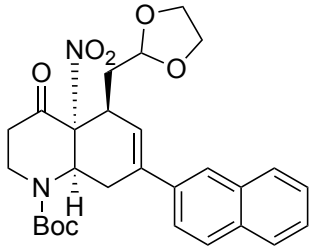
C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk139¥hmk139 C-end.als

DFILE hmk139 C-end.als
COMNT single pulse decoupled gated NOE
DATIM 2019-03-08 03:20:24
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 6822
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 128.06 ppm
BF 0.10 Hz
RGAIN 56



196.030 154.119 137.322 134.098 133.592 132.810 128.546 128.394 128.251 128.165 128.117 128.060 127.974 127.869 126.973 126.877 126.534 126.295 124.655 124.588 124.254 103.566 97.947 81.198 65.145 64.849 57.314 40.422 39.430 38.218 34.537 31.904 28.995 28.394 22.957 14.134

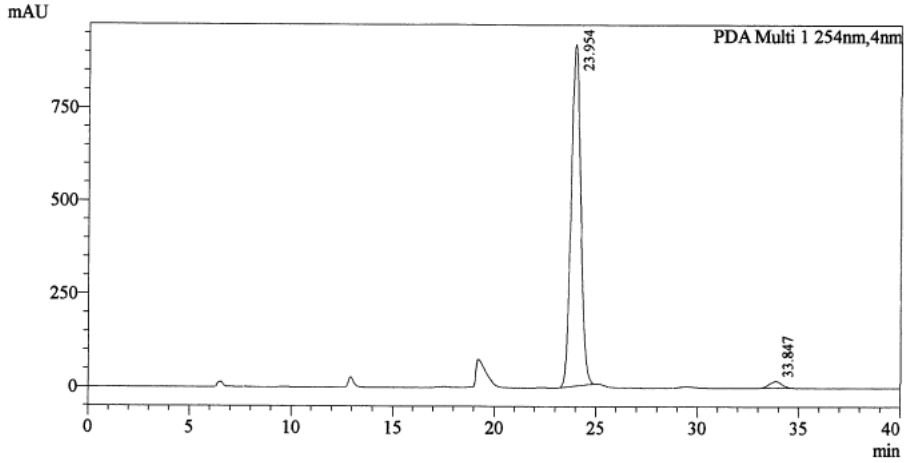
=== Shimadzu LabSolutions Report ===



8

Sample Name	: hmk140 ee major				
Sample ID	: inoshita				
Data Filename	: hmk140 ee majori.lcd				
Method Filename	: 10%iPrOH-Hex-flow0.5.lcm				
Batch Filename	:				
Vial#	: 1-1			Sample Type	: ¬¢'m
Injection Volume	: 20 uL				
Date Acquired	: 2018/08/07 13:01:56	Acquired by		: System Administrator	
Date Processed	: 2019/03/13 20:40:55	Processed by		: System Administrator	

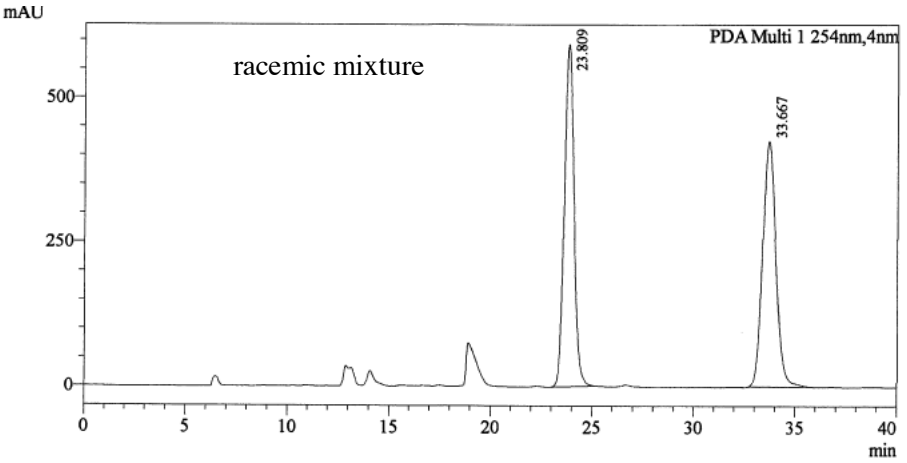
<Chromatogram>



<Peak Table>

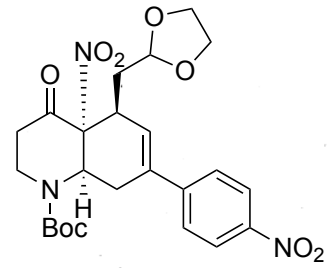
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Name
1	23.954	29999969	916988	97.472	
2	33.847	777959	18340	2.528	
‡Œv		30777929	935327		

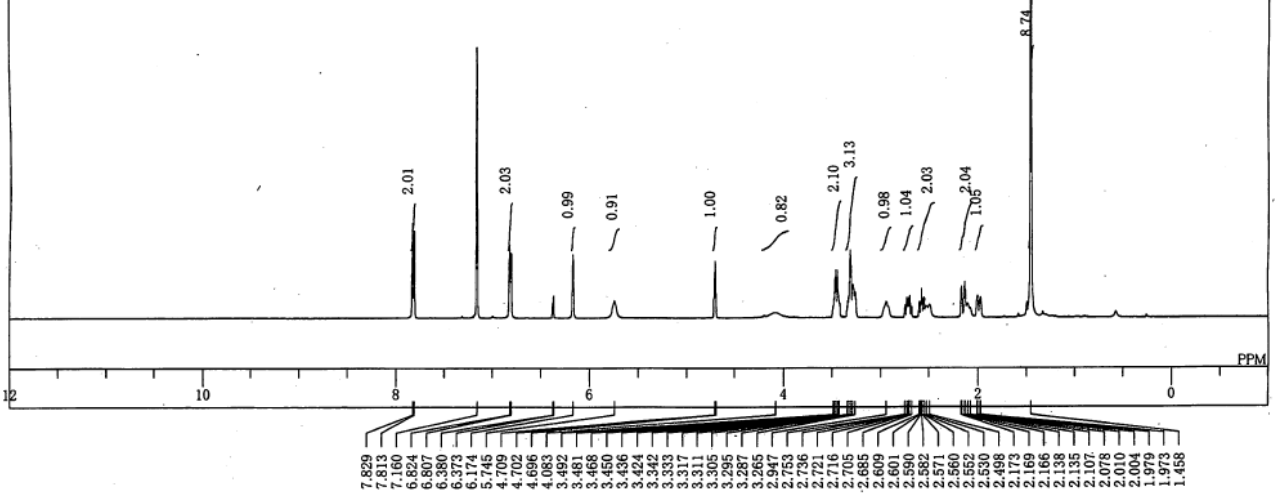


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk57¥hmk57 H benz-end.als

DFILE hmk57 H benz-end.als
COMNT single_pulse
DATIM 2019-02-15 22:07:34
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.10 Hz
RGAIN 42



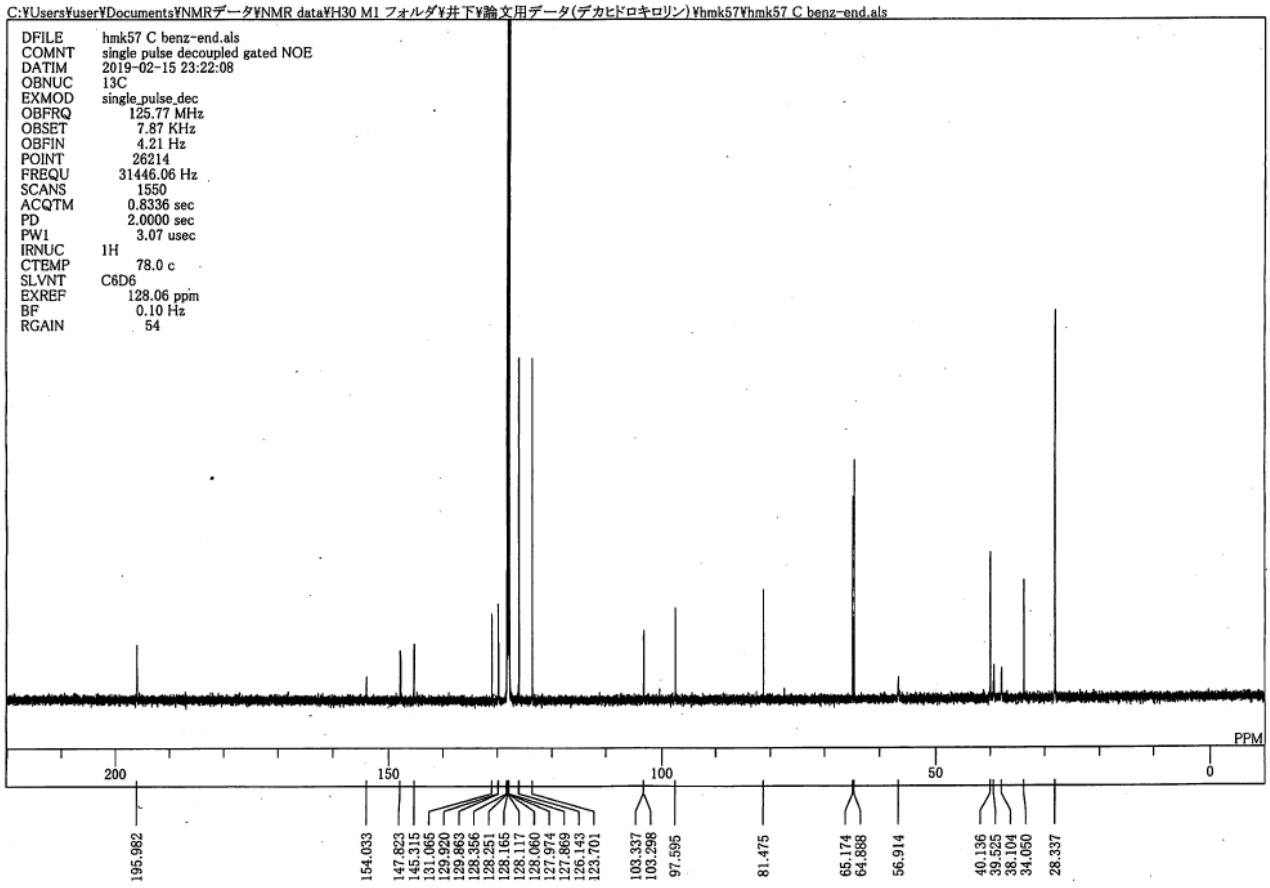
9



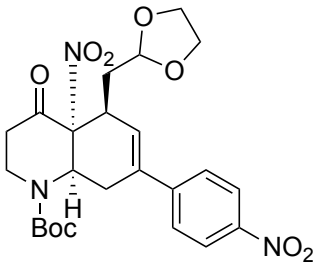
7.829 7.813 7.160 6.824 6.807 6.380 6.373 6.174 5.745 4.709 4.702 4.696 4.083 3.492 3.481 3.468 3.450 3.436 3.424 3.342 3.333 3.317 3.311 3.305 3.295 3.287 3.265 2.947 2.753 2.736 2.721 2.716 2.705 2.685 2.609 2.601 2.590 2.582 2.571 2.560 2.552 2.530 2.498 2.173 2.169 2.166 2.138 2.135 2.107 2.078 2.010 2.004 1.979 1.973 1.458

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk57¥hmk57_C benz-end.als

DFILE hmk57 C benz-end.als
COMNT single pulse decoupled gated NOE
DATIM 2019-02-15 23:22:08
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1550
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 128.06 ppm
BF 0.10 Hz
RGAIN 54



195.982 154.033 147.823 145.315 131.065 129.920 129.863 128.356 128.251 128.165 128.117 128.060 127.974 127.869 126.143 123.701 103.337 103.298 97.595 81.475 65.174 64.888 56.914 40.136 39.525 38.104 34.050 28.337

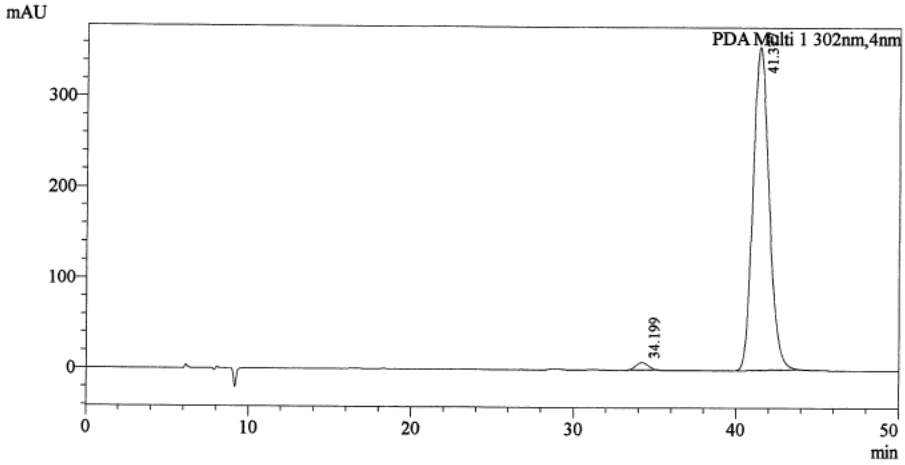


9

=== Shimadzu LabSolutions Report ===

Sample Name	: hmk56 ee major 40%		
Sample ID	: inoshita		
Data Filename	: hmk56 ee major 40%.lcd		
Method Filename	: 40%iproh-Hex-flow0.5.lcm		
Batch Filename	:		
Vial#	: 1-1	Sample Type	: ¬¢'m
Injection Volume	: 2000 uL		
Date Acquired	: 2018/01/23 16:52:25 Acquired by	: System Administrator	
Date Processed	: 2018/01/23 20:55:51 Processed by	: System Administrator	

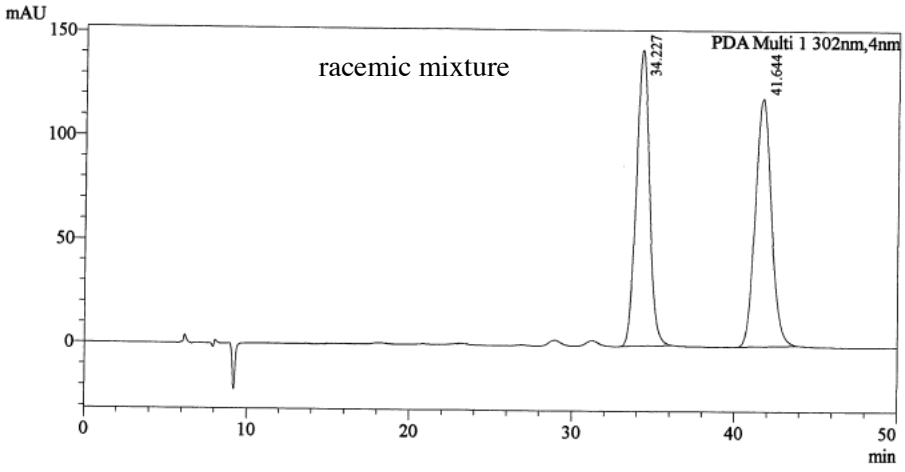
<Chromatogram>

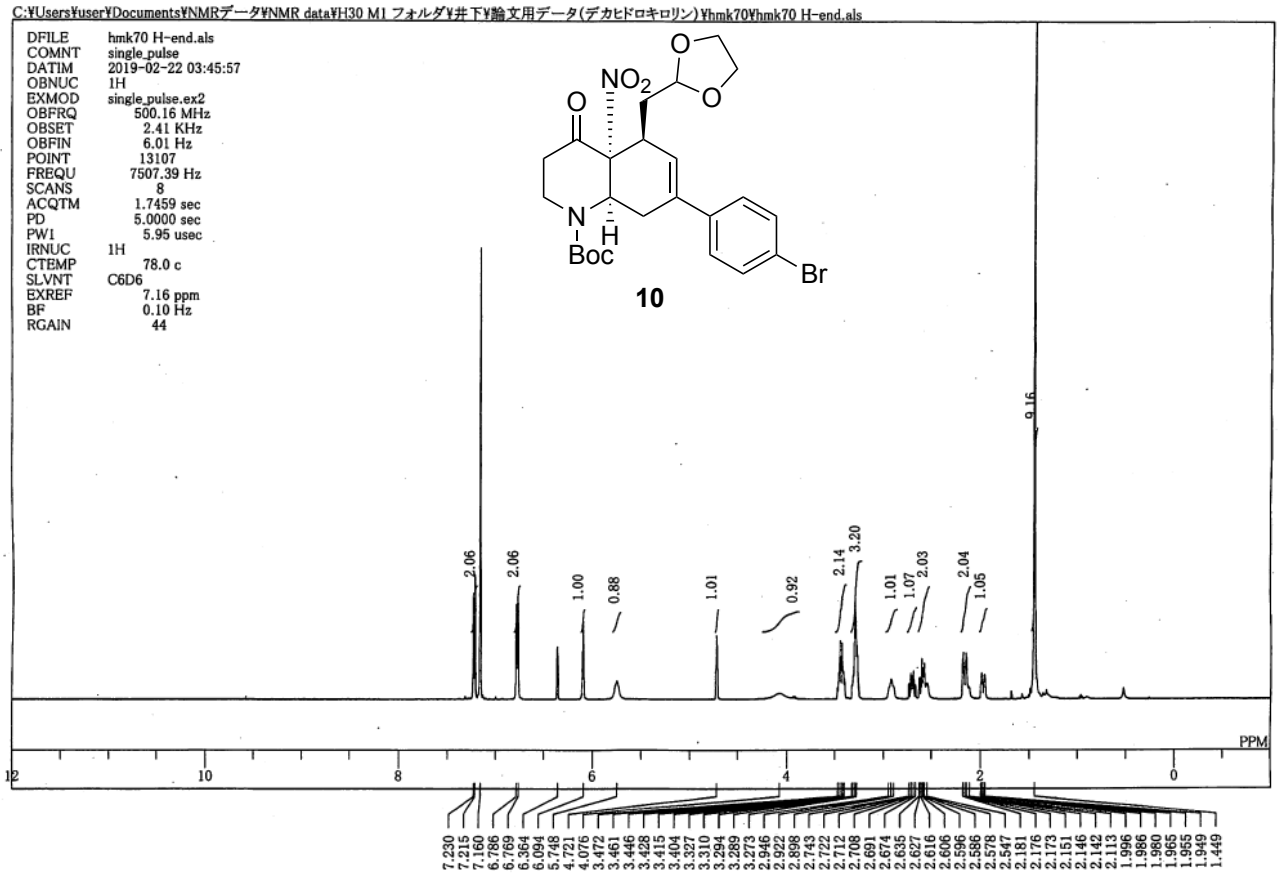


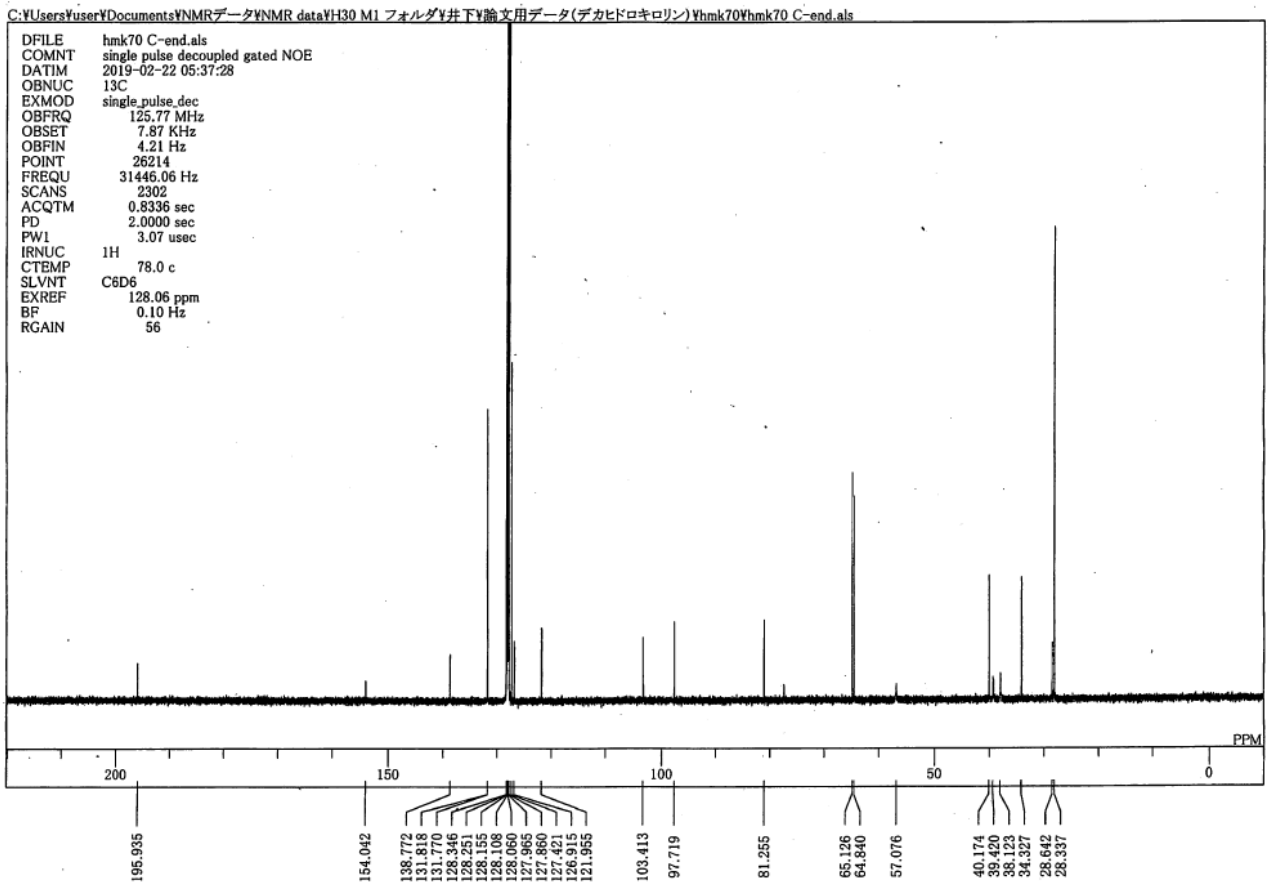
<Peak Table>

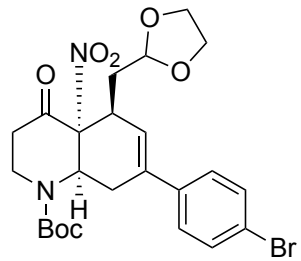
PDA Ch1 302nm

Peak#	Ret. Time	Area	Height	Conc.	Name
1	34.199	422568	8244	1.680	
2	41.377	24735839	356995	98.320	
‡Œv		25158407	365239		




C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk70¥hmk70 H-end.als
DFILE hmk70 H-end.als
COMNT single_pulse
DATIM 2019-02-22 03:45:57
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.10 Hz
RGAIN 44
NO2
O
N
H
Boc
Br
10
PPM


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk70¥hmk70 C-end.als
DFILE hmk70 C-end.als
COMNT single pulse decoupled gated NOE
DATIM 2019-02-22 05:37:28
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 2302
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 128.06 ppm
BF 0.10 Hz
RGAIN 56
PPM



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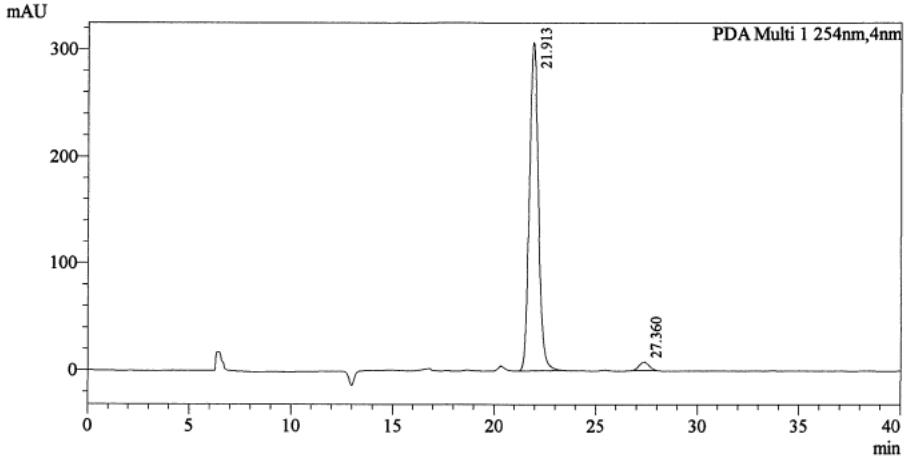
=== Shimadzu LabSolutions Report ===

Sample Name	: hmk70 ee major		
Sample ID	: inoshita		
Data Filename	: hmk70 ee major.lcd		
Method Filename	: 10%iPrOH-Hex-flow0.5.lcm		
Batch Filename	:		
Vial#	: 1-1	Sample Type	: –¢'m
Injection Volume	: 2000 uL		
Date Acquired	: 2018/02/10 12:08:06 Acquired by	: System Administrator	
Date Processed	: 2019/03/13 23:20:41 Processed by	: System Administrator	

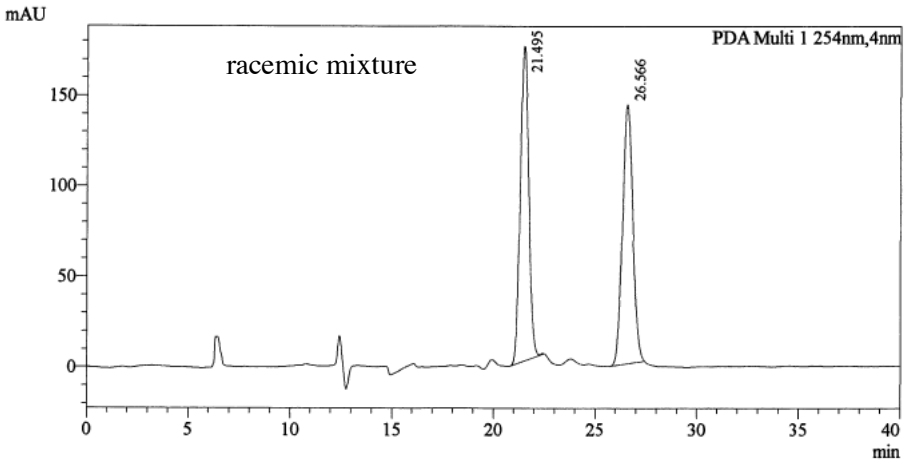
<Chromatogram>



<Peak Table>

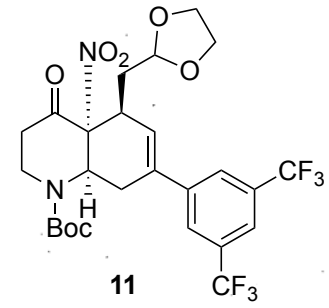
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Name
1	21.913	9391132	306629	97.296	
2	27.360	260957	7640	2.704	
‡Œv		9652089	314269		



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキノリン)¥hmk135¥hmk135 H-end.als

DFILE	hmk135 H-end.als
COMNT	single_pulse
DATIM	2019-02-22 00:46:30
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.95 usec
IRNUC	1H
CTEMP	78.0 c
SLVNT	C6D6
EXREF	7.16 ppm
BF	0.10 Hz
RGAIN	50



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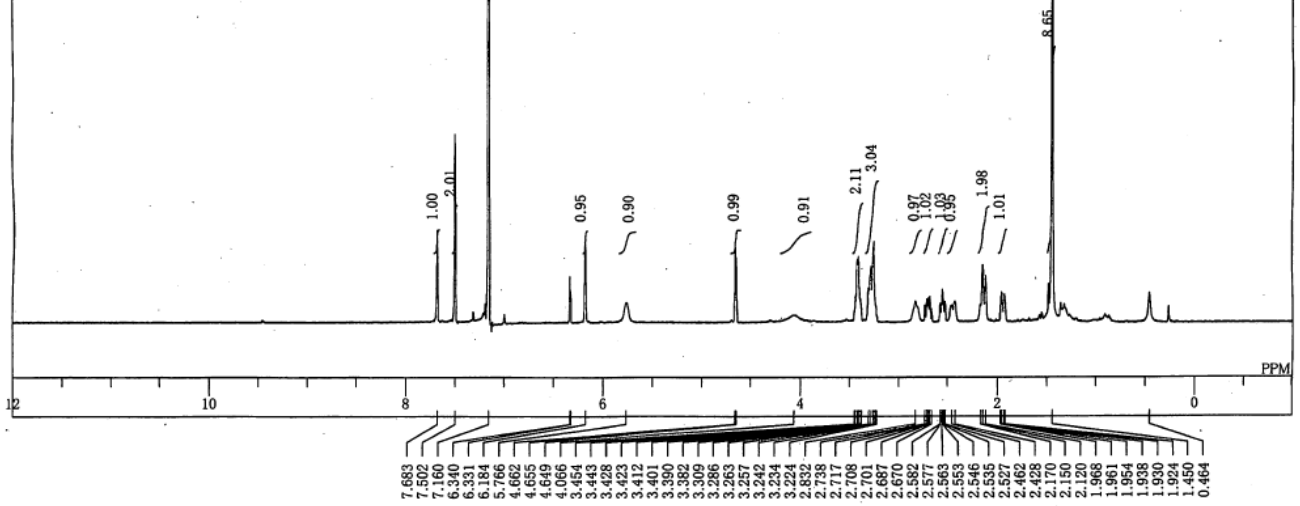
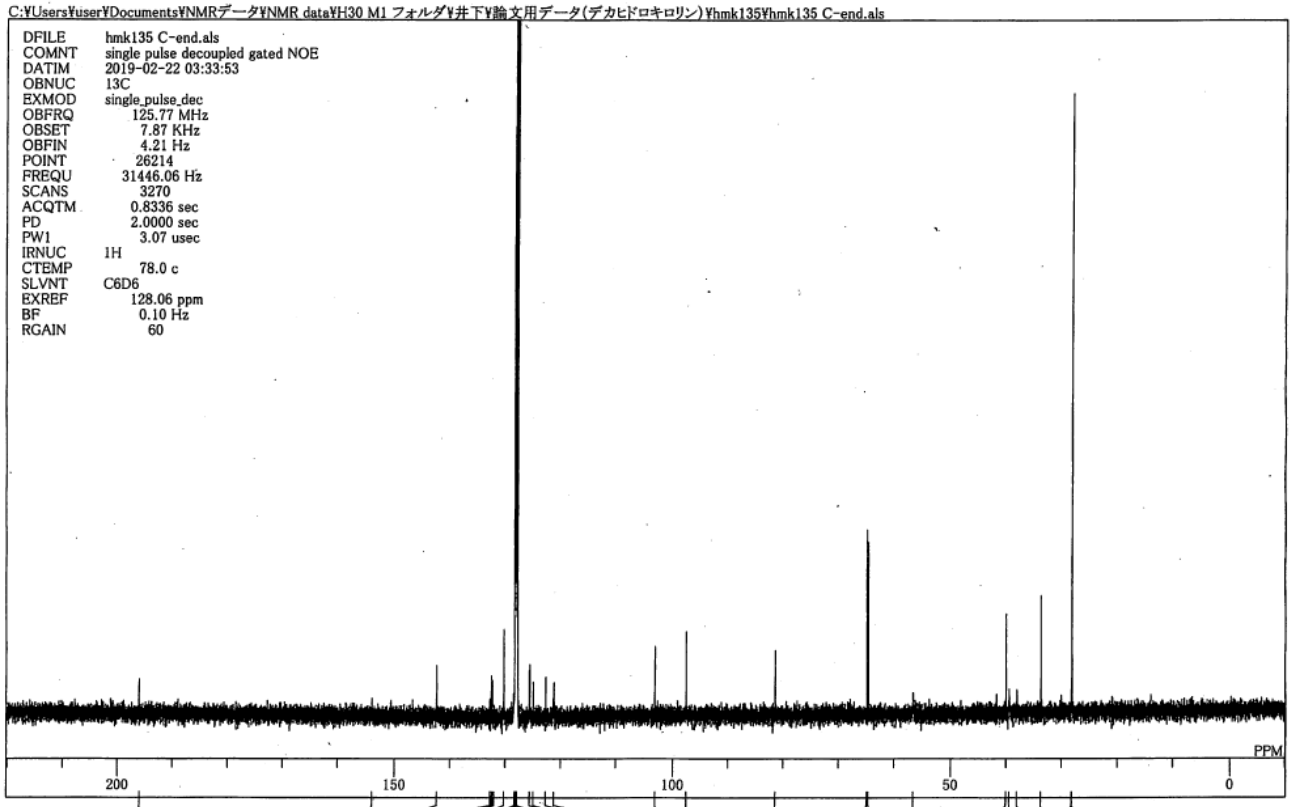


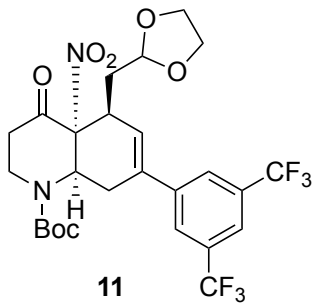
7.683 7.502 7.160 6.340 6.331 6.184 5.766 4.662 4.655 4.649 4.066 3.454 3.443 3.428 3.423 3.412 3.401 3.390 3.382 3.309 3.286 3.263 3.257 3.242 3.234 3.224 2.832 2.738 2.717 2.708 2.701 2.687 2.670 2.582 2.577 2.563 2.553 2.546 2.535 2.527 2.462 2.428 2.170 2.150 2.120 1.968 1.961 1.954 1.938 1.930 1.924 1.450 0.464

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキノリン)¥hmk135¥hmk135 C-end.als

DFILE	hmk135 C-end.als
COMNT	single pulse decoupled gated NOE
DATIM	2019-02-22 03:33:53
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	3270
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.07 usec
IRNUC	1H
CTEMP	78.0 c
SLVNT	C6D6
EXREF	128.06 ppm
BF	0.10 Hz
RGAIN	60



195.963 153.909 142.329 132.791 132.514 132.257 131.990 130.273 128.565 128.260 128.174 128.127 128.070 127.984 127.879 125.656 124.998 122.833 121.383 121.355 103.213 97.633 81.561 65.126 64.859 56.828 40.098 39.516 38.133 33.898 28.327 28.270



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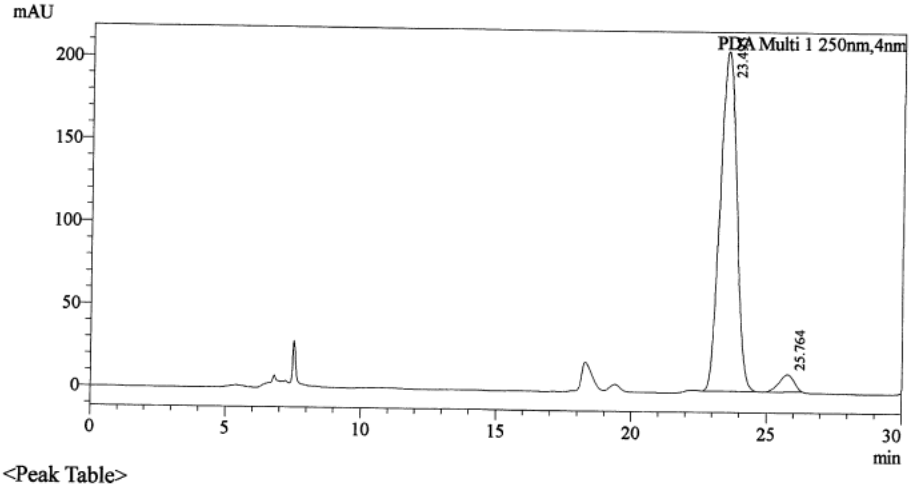
=== Shimadzu LabSolutions Report ===

Sample Name	: hmk133 ee major 3		
Sample ID	: inoshita		
Data Filename	: hmk133 ee major 3.lcd		
Method Filename	: 2%iPrOH-Hex-flow0.2.lcm		
Batch Filename	:		
Vial#	: 1-1	Sample Type	: ¬ê'm
Injection Volume	: 20 uL		
Date Acquired	: 2018/07/25 16:19:33 Acquired by	: System Administrator	
Date Processed	: 2018/07/25 16:53:03 Processed by	: System Administrator	

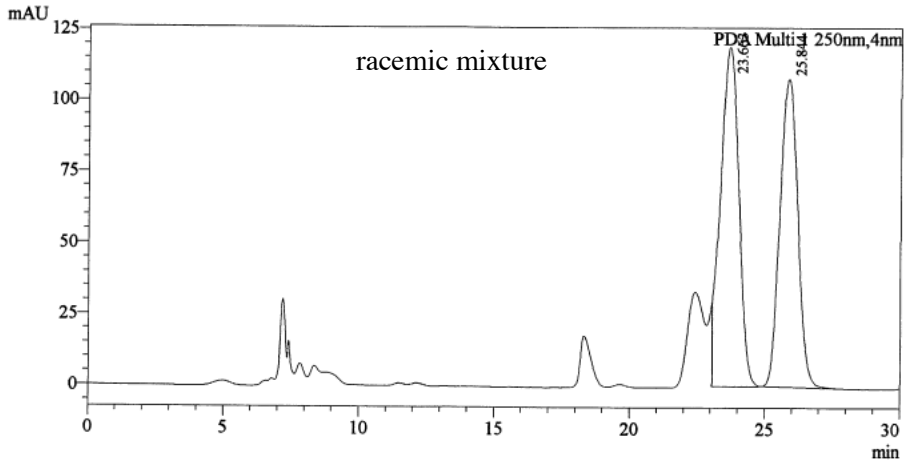
<Chromatogram>

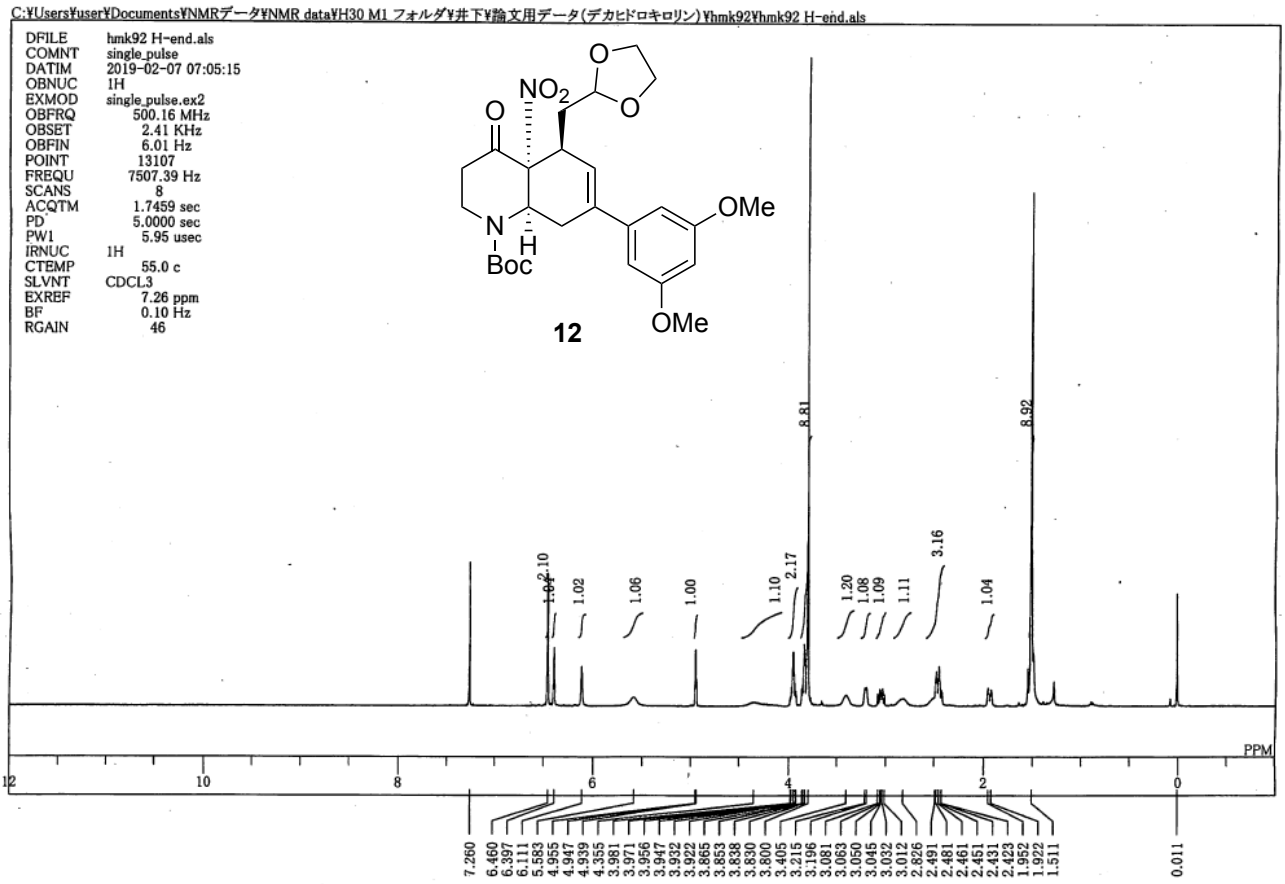


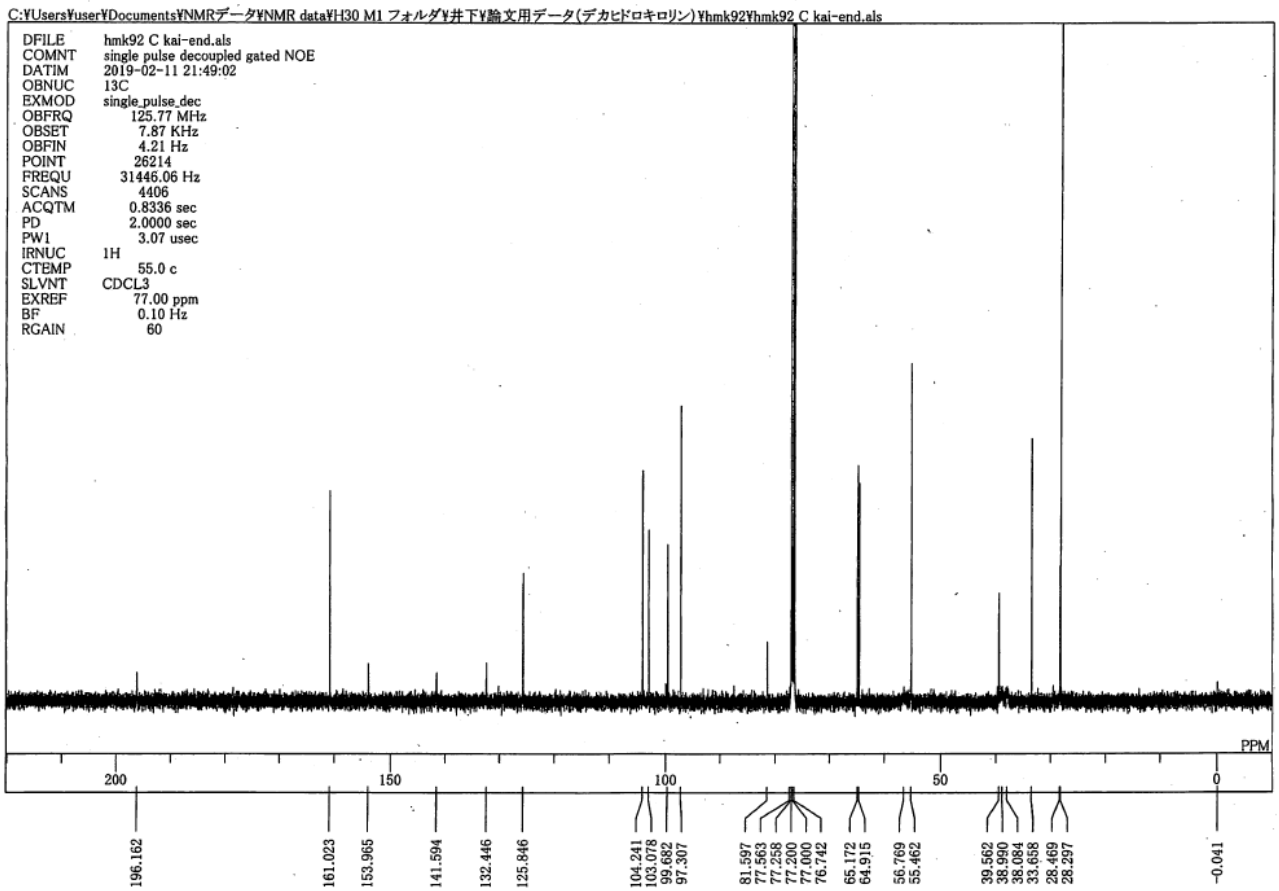
<Peak Table>

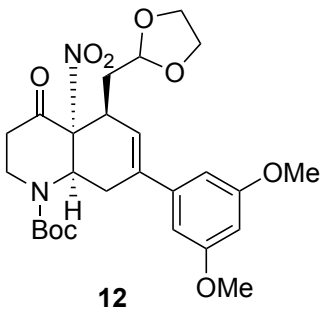
PDA Ch1 250nm

Peak#	Ret. Time	Area	Height	Conc.	Name
1	23.493	8798419	205986	95.528	
2	25.764	411904	10598	4.472	
‡Œv		9210324	216584		




C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk92¥hmk92 H-end.als
DFILE hmk92 H-end.als
COMNT single_pulse
DATIM 2019-02-07 07:05:15
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 55.0 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 46
NO2
O
O
O
OMe
N
H
Boc
OMe
12
8.81
8.92
3.16
2.17
2.10
1.02
1.06
1.00
1.10
1.20
1.08
1.09
1.11
1.04
PPM
12
10
8
6
4
2
0
7.260
6.460
6.397
6.111
5.583
4.955
4.947
4.939
4.355
3.981
3.971
3.956
3.947
3.932
3.922
3.865
3.853
3.838
3.830
3.800
3.405
3.215
3.196
3.081
3.063
3.050
3.045
3.032
3.012
2.826
2.491
2.481
2.461
2.451
2.431
2.423
1.952
1.922
1.511
0.011


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk92¥hmk92 C kai-end.als
DFILE hmk92 C kai-end.als
COMNT single pulse decoupled gated NOE
DATIM 2019-02-11 21:49:02
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 4406
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 55.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 60
PPM
200
150
100
50
0
196.162
161.023
153.965
141.594
132.446
125.846
104.241
103.078
99.682
97.307
81.597
77.563
77.258
77.200
77.000
76.742
65.172
64.915
56.769
55.462
39.562
38.990
38.084
33.658
28.469
28.297
-0.041



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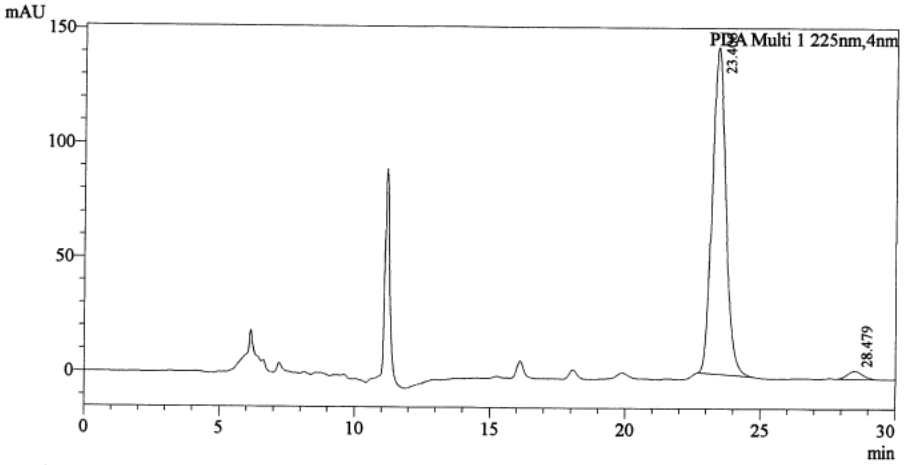
=== Shimadzu LabSolutions Report ===

Sample Name	: hmk92 ee major 3		
Sample ID	: inoshita		
Data Filename	: hmk92 ee major 3.lcd		
Method Filename	: 20%iPrOH-Hex-flow0.5.lcm		
Batch Filename	:		
Vial#	: 1-1	Sample Type	: ¬¢'m
Injection Volume	: 2000 uL		
Date Acquired	: 2018/04/19 15:10:16 Acquired by	: System Administrator	
Date Processed	: 2019/03/14 16:24:25 Processed by	: System Administrator	

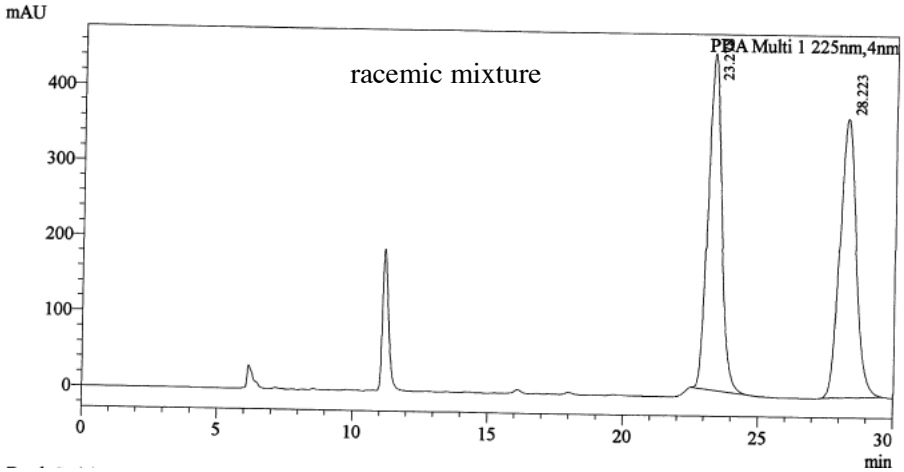
<Chromatogram>



<Peak Table>

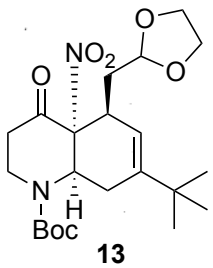
PDA Ch1 225nm

Peak#	Ret. Time	Area	Height	Conc.	Name
1	23.406	5002570	143002	97.397	
2	28.479	133699	3475	2.603	
‡Œv		5136268	146476		



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk166¥hmk166 H-end.als

DFILE hmk166 H-end.als
COMNT single_pulse
DATIM 2019-02-20 04:42:46
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.10 Hz
RGAIN 50

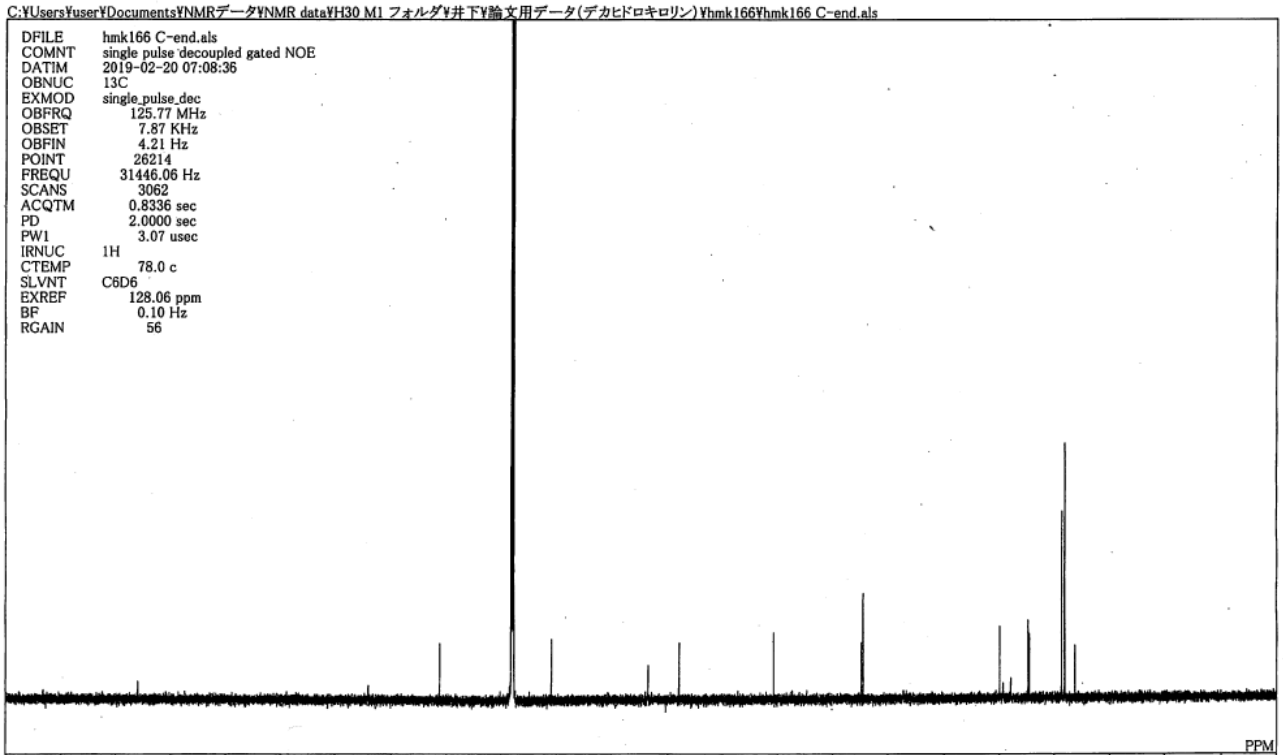


13

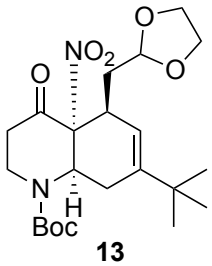
7.160
5.672 5.635 4.762 4.754 4.746 4.061 3.462 3.450 3.435 3.421 3.407 3.396 3.309 3.297 3.278 3.245 3.225 3.050 3.041 3.021 3.004 2.994 2.720 2.701 2.686 2.670 2.651 2.614 2.606 2.594 2.584 2.576 2.564 2.556 2.445 2.410 2.199 2.193 2.168 2.164 2.035 1.993 1.961 1.444 0.887

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk166¥hmk166 C-end.als

DFILE hmk166 C-end.als
COMNT single pulse decoupled gated NOE
DATIM 2019-02-20 07:08:36
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 3062
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 128.06 ppm
BF 0.10 Hz
RGAIN 56



195.973
154.185
141.347
128.556
128.356
128.260
128.165
128.117
128.060
127.974
127.869
121.059
103.604
98.062
80.950
65.078
64.773
57.476
40.078
39.487
38.104
35.033
34.794
28.871
28.356
26.515

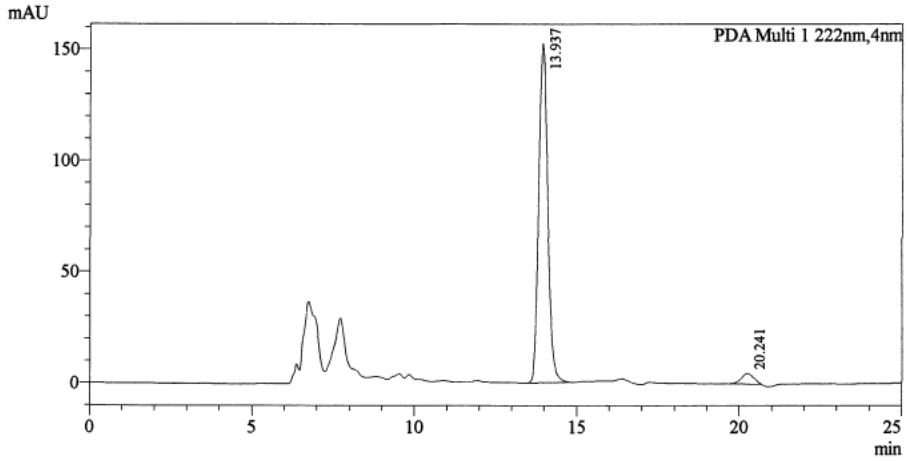


13

=== Shimadzu LabSolutions Report ===

Sample Name	: hmk166 ee major			
Sample ID	: inoshita			
Data Filename	: hmk166 ee major.lcd			
Method Filename	: 10%iPrOH-Hex-flow0.5.lcm			
Batch Filename	:			
Vial#	: 1-1		Sample Type	: ¬¢'m
Injection Volume	: 20 uL			
Date Acquired	: 2018/10/15 4:38:31	Acquired by	: System Administrator	
Date Processed	: 2018/10/15 5:11:29	Processed by	: System Administrator	

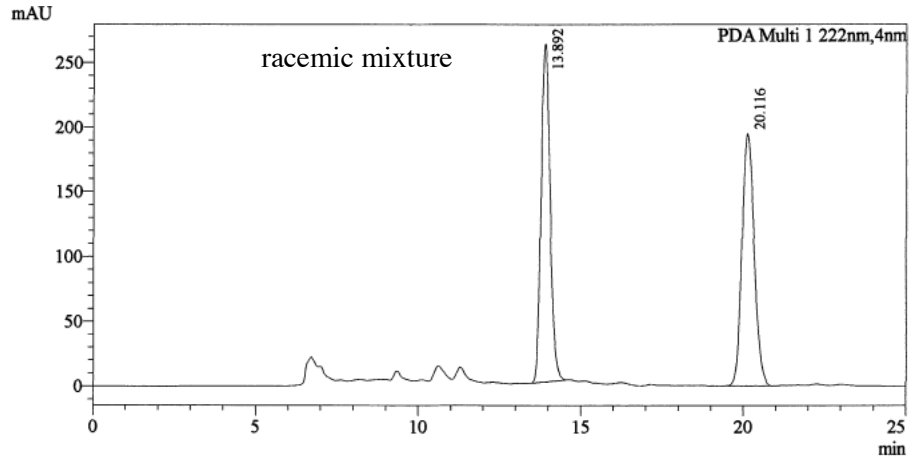
<Chromatogram>



<Peak Table>

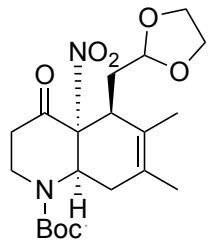
PDA Ch1 222nm

Peak#	Ret. Time	Area	Height	Conc.	Name
1	13.937	2946738	152526	96.042	
2	20.241	121450	4663	3.958	
‡Œv		3068189	157189		



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk203¥hmk203 h-end.als

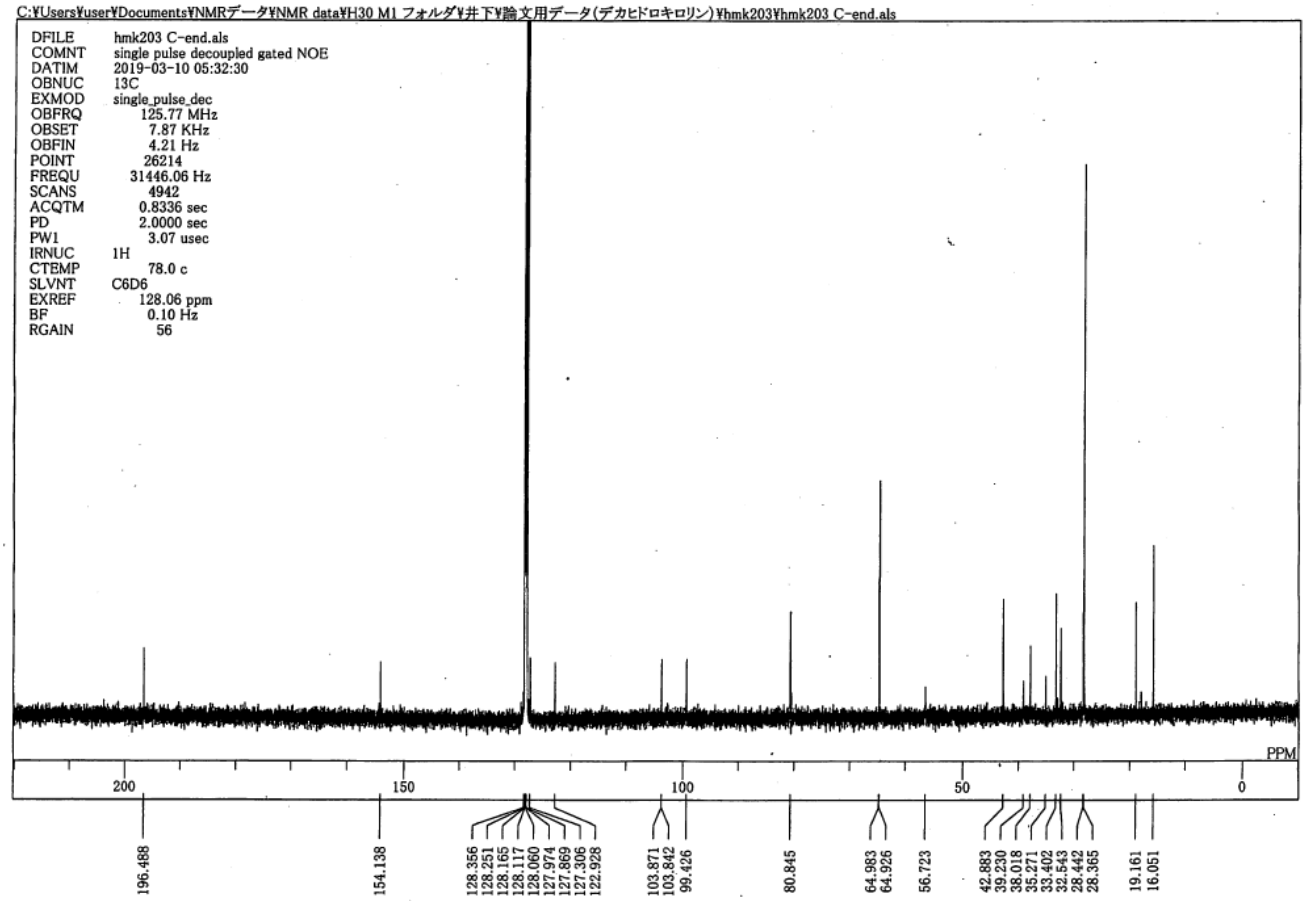
DFILE	hmk203 h-end.als
COMNT	single_pulse
DATIM	2019-03-10 01:37:60
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.95 usec
IRNUC	1H
CTEMP	78.0 c
SLVNT	C6D6
EXREF	7.16 ppm
BF	0.10 Hz
RGAIN	50



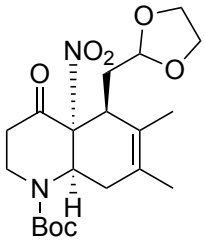
14

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk203¥hmk203 C-end.als

DFILE	hmk203 C-end.als
COMNT	single pulse decoupled gated NOE
DATIM	2019-03-10 05:32:30
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	4942
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.07 usec
IRNUC	1H
CTEMP	78.0 c
SLVNT	C6D6
EXREF	128.06 ppm
BF	0.10 Hz
RGAIN	56



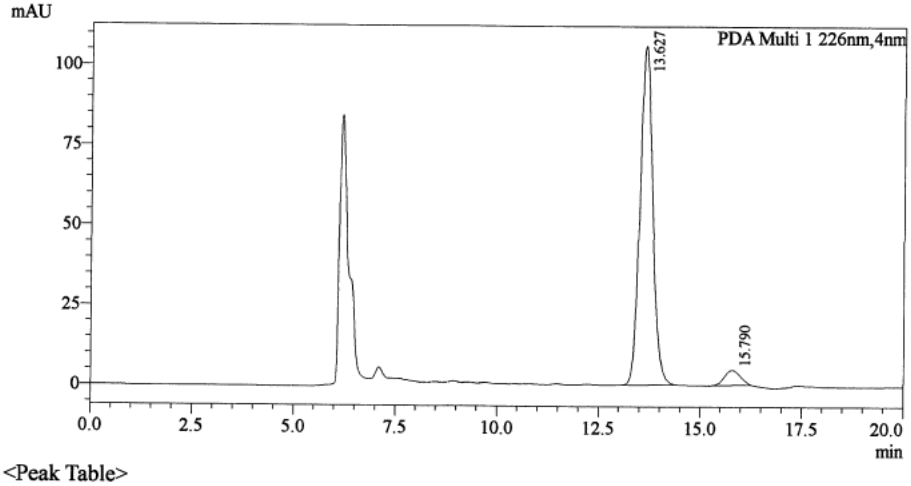
=== Shimadzu LabSolutions Report ===



14

Sample Name	: hmk83 mouikkai ee major 3			
Sample ID	: inoshita			
Data Filename	: hmk83 mouikkai ee major OD-H.lcd			
Method Filename	: 10%iPrOH-Hex-flow0.5.lcm			
Batch Filename	:			
Vial#	: 1-1		Sample Type	: -¢'m
Injection Volume	: 20 uL			
Date Acquired	: 2018/10/19 1:24:54	Acquired by	: System Administrator	
Date Processed	: 2018/10/19 2:38:58	Processed by	: System Administrator	

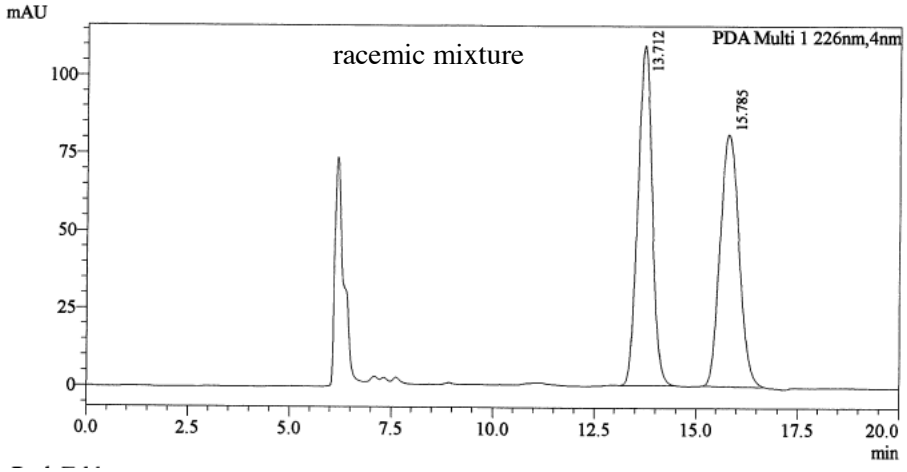
<Chromatogram>



<Peak Table>

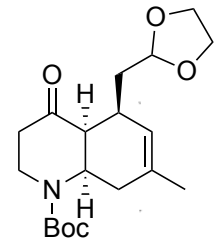
PDA Ch1 226nm

Peak#	Ret. Time	Area	Height	Conc.	Name
1	13.627	2310619	105867	94.815	
2	15.790	126348	4654	5.185	
‡Œv		2436967	110521		



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk206 cis¥hmkdenitro_H end.als

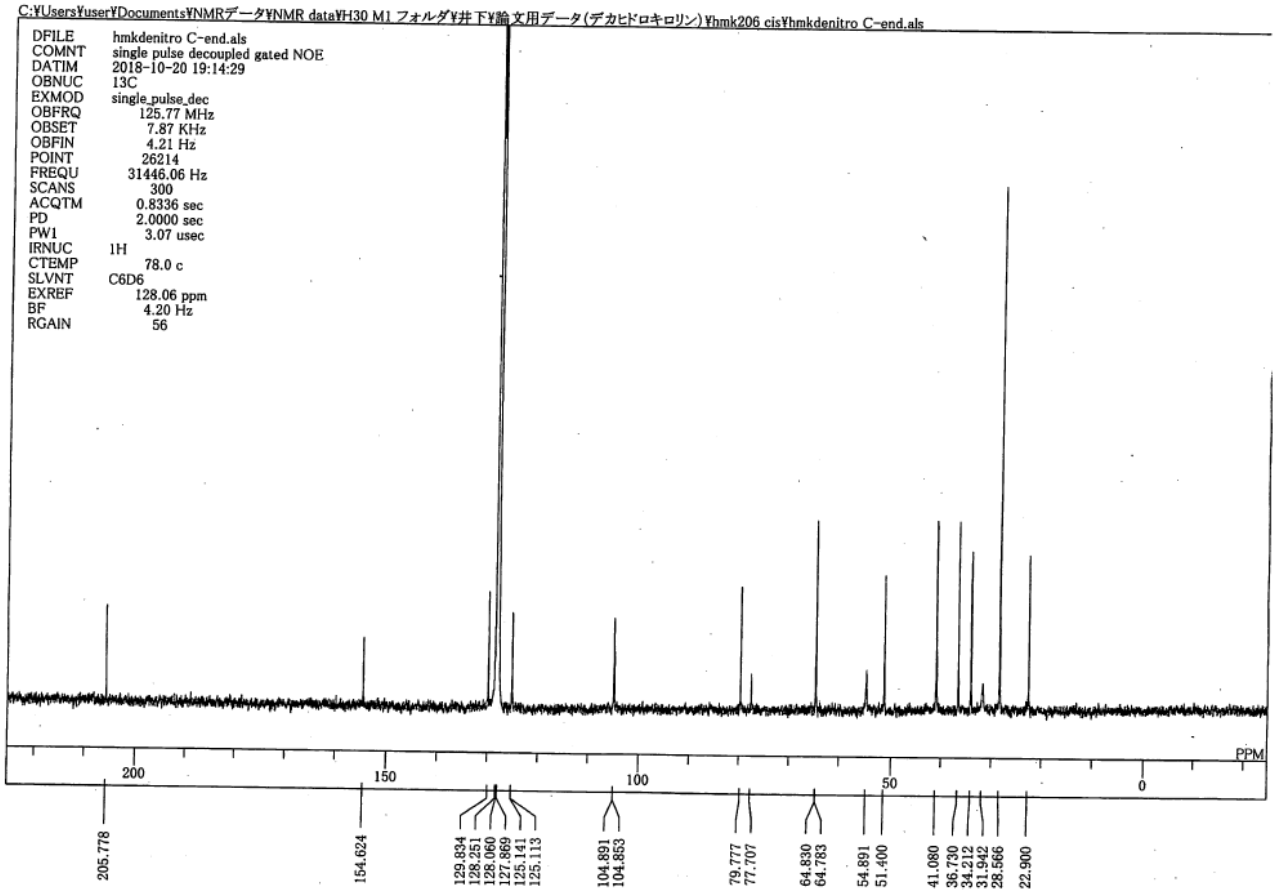
DFILE	hmkdenitro H end.als
COMNT	single_pulse
DATIM	2018-10-20 18:58:29
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.95 usec
IRNUC	1H
CTEMP	78.0 c
SLVNT	C6D6
EXREF	7.16 ppm
BF	4.20 Hz
RGAIN	38

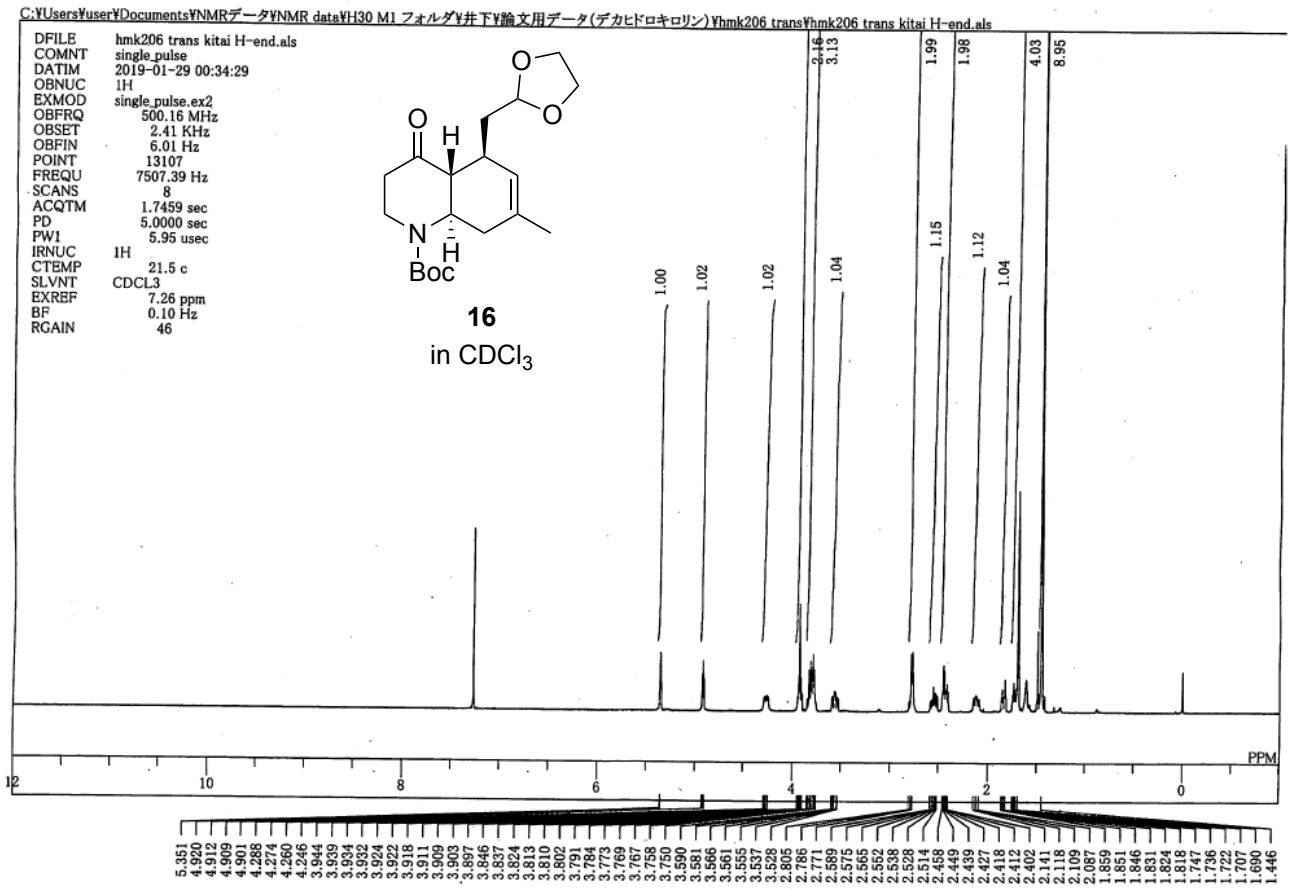


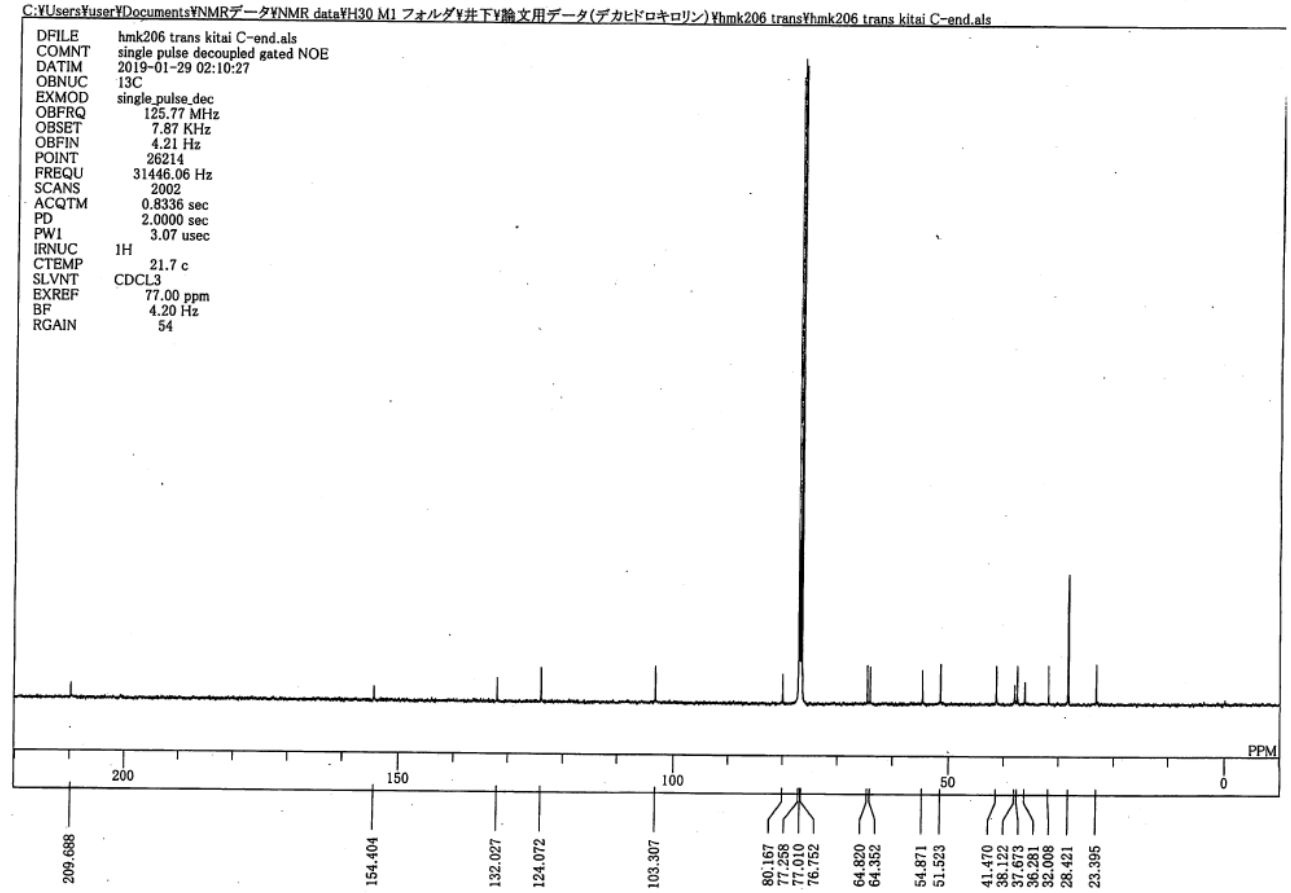
15

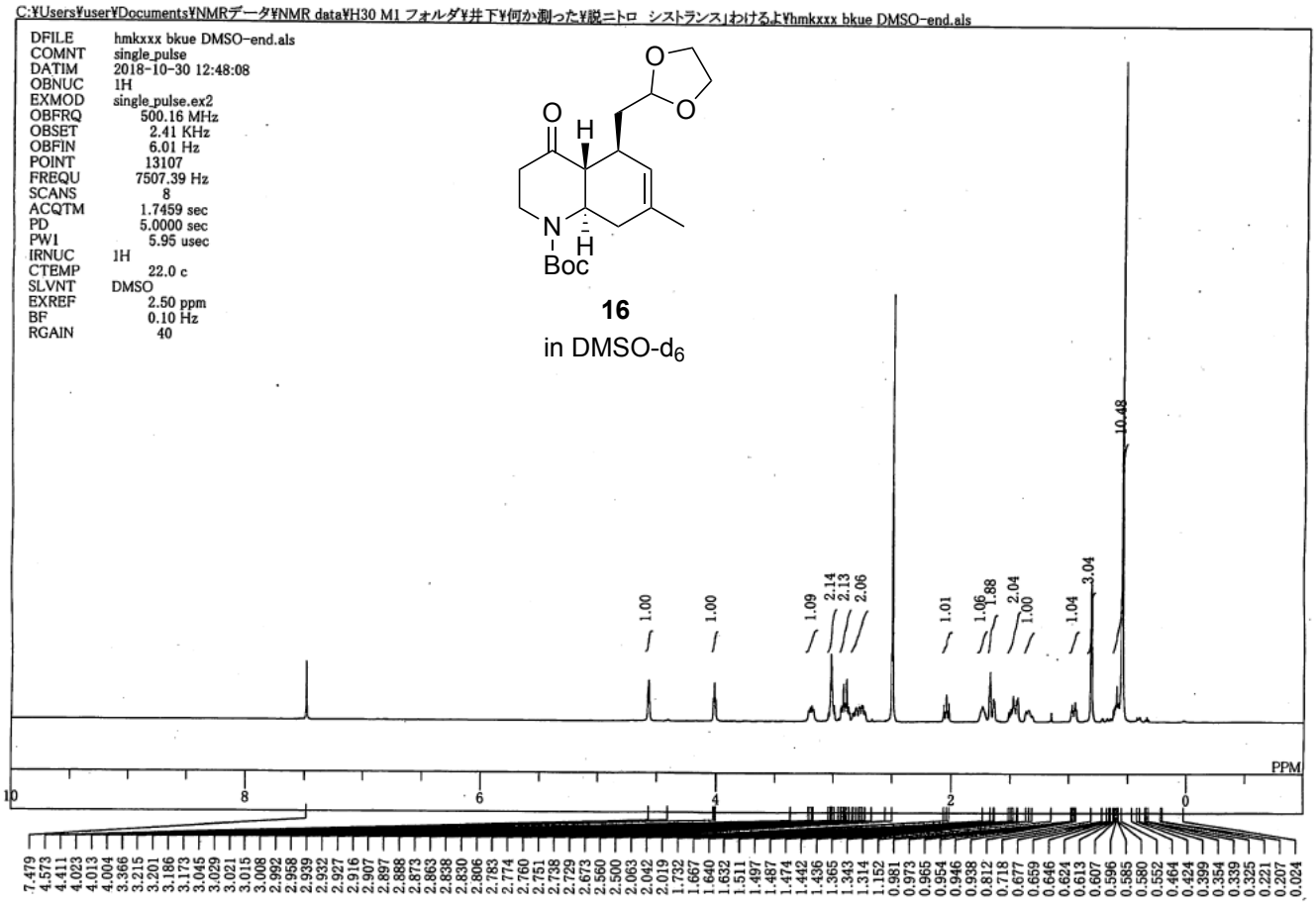
C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk206 cis¥hmkdenitro C-end.als

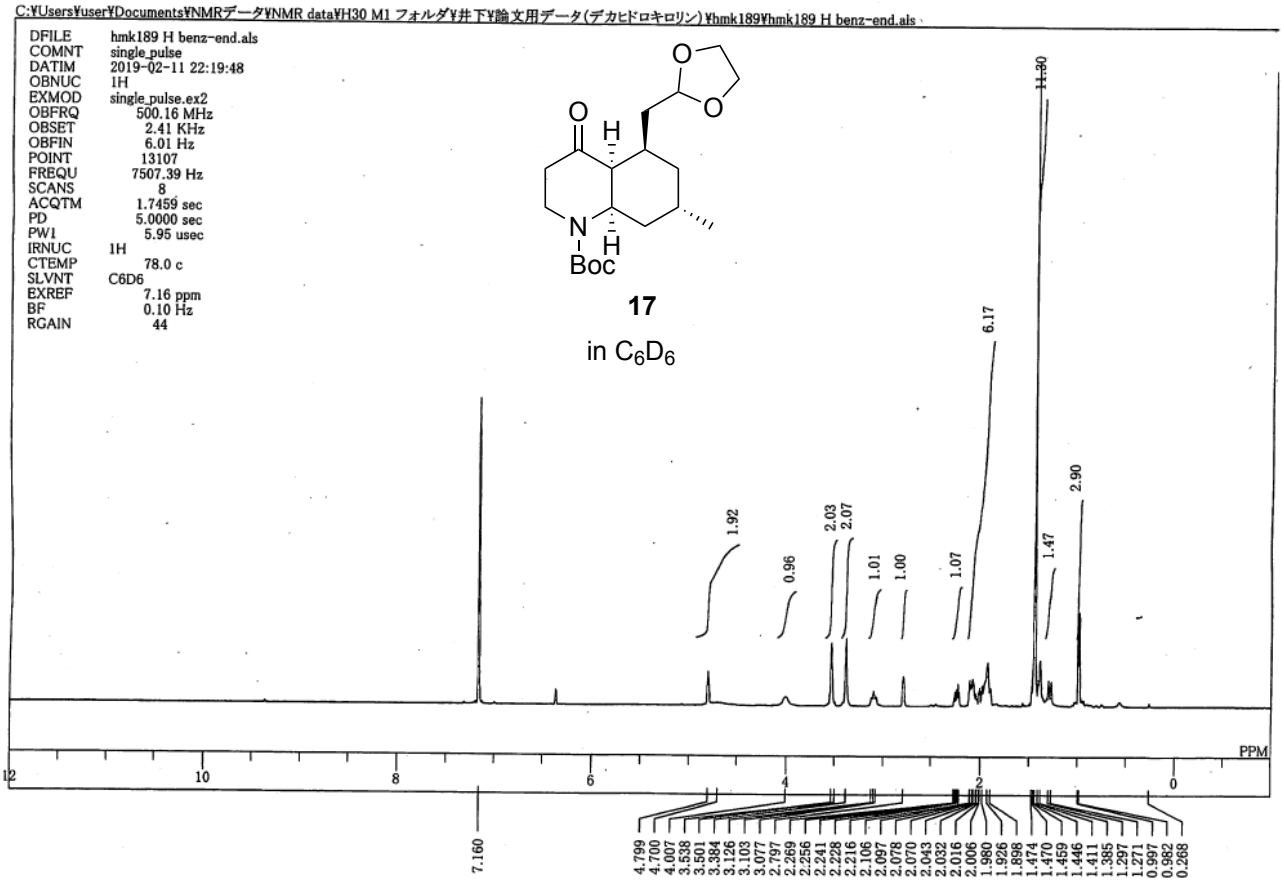
DFILE	hmkdenitro C-end.als
COMNT	single pulse decoupled gated NOE
DATIM	2018-10-20 19:14:29
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	300
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.07 usec
IRNUC	1H
CTEMP	78.0 c
SLVNT	C6D6
EXREF	128.06 ppm
BF	4.20 Hz
RGAIN	56

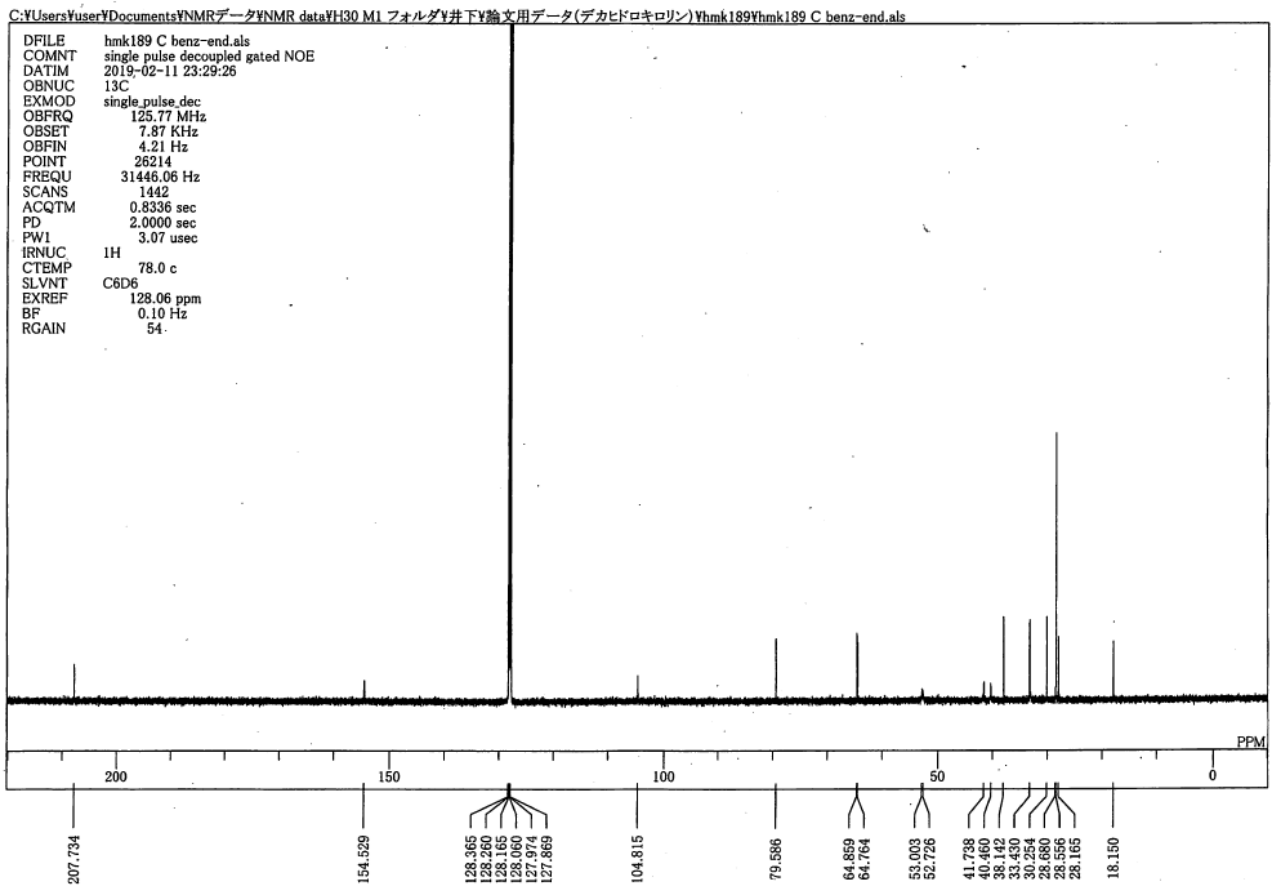



C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk206 trans¥hmk206 trans kitai H-end.als
DFILE hmk206 trans kitai H-end.als
COMNT single_pulse
DATIM 2019-01-29 00:34:29
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 46
O
H
O
O
N
H
Boc
16
in CDCl3
1.00
1.02
1.02
2.46
3.13
1.04
1.99
1.15
1.98
1.12
1.04
4.03
8.95
PPM
12
10
8
6
4
2
0
5.351
4.920
4.912
4.909
4.901
4.288
4.274
4.260
4.246
3.944
3.939
3.934
3.932
3.924
3.922
3.918
3.911
3.909
3.903
3.897
3.846
3.837
3.824
3.813
3.810
3.802
3.791
3.784
3.773
3.769
3.767
3.758
3.750
3.590
3.581
3.566
3.561
3.555
3.537
3.528
2.805
2.786
2.771
2.589
2.575
2.565
2.552
2.538
2.528
2.514
2.458
2.449
2.439
2.427
2.418
2.412
2.402
2.141
2.118
2.109
2.087
1.859
1.851
1.846
1.831
1.824
1.818
1.747
1.736
1.722
1.707
1.690
1.446


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk206 trans¥hmk206 trans kitai C-end.als
DFILE hmk206 trans kitai C-end.als
COMNT single pulse decoupled gated NOE
DATIM 2019-01-29 02:10:27
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 2002
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 4.20 Hz
RGAIN 54
PPM
200
150
100
50
0
209.688
154.404
132.027
124.072
103.307
80.167
77.258
77.010
76.752
64.820
64.352
54.871
51.523
41.470
38.122
37.673
36.281
32.008
28.421
23.395

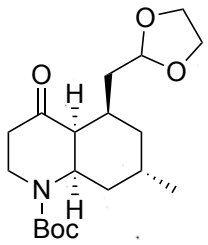

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥何か測った¥脱ニトロ シストランス¥わける.fid¥hmkxxx bkue DMSO-end.als
DFILE hmkxxx bkue DMSO-end.als
COMNT single_pulse
DATIM 2018-10-30 12:48:08
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT DMSO
EXREF 2.50 ppm
BF 0.10 Hz
RGAIN 40
O
O
O
H
N
H
Boc
16
in DMSO-d6
1.00
1.00
1.09
2.14
2.13
2.06
1.01
1.06
1.88
2.04
1.00
1.04
3.04
10.48
PPM
10
8
6
4
2
0


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk189¥hmk189 H benz-end.als
DFILE hmk189 H benz-end.als
COMNT single_pulse
DATIM 2019-02-11 22:19:48
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.10 Hz
RGAIN 44
O
O
O
H
N
H
Boc
17
in C6D6
11.30
6.17
2.90
2.03
2.07
1.92
1.47
1.07
0.96
1.01
1.00
PPM
12
10
8
6
4
2
0
7.160
4.799
4.700
4.007
3.538
3.501
3.384
3.126
3.103
3.077
2.797
2.269
2.256
2.241
2.228
2.216
2.106
2.097
2.078
2.070
2.043
2.032
2.016
2.006
1.980
1.926
1.898
1.474
1.470
1.459
1.446
1.411
1.385
1.297
1.271
0.997
0.982
0.268


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk189¥hmk189 C benz-end.als
DFILE hmk189 C benz-end.als
COMNT single pulse decoupled gated NOE
DATIM 2019-02-11 23:29:26
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1442
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 78.0 c
SLVNT C6D6
EXREF 128.06 ppm
BF 0.10 Hz
RGAIN 54
PPM
200
150
100
50
0
207.734
154.529
128.365
128.260
128.165
128.060
127.974
127.869
104.815
79.586
64.859
64.764
53.003
52.726
41.738
40.460
38.142
33.430
30.254
28.680
28.556
28.165
18.150

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥208¥pyri¥hmk208 pyri 95-end.als

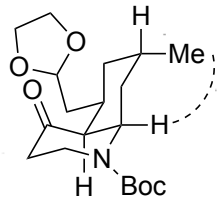
DFILE	hmk208 pyri 95-end.als
COMNT	single_pulse
DATIM	2019-02-28 21:34:28
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.95 usec
IRNUC	1H
CTEMP	95.0 c
SLVNT	C5D5N
EXREF	8.60 ppm
BF	0.12 Hz
RGAIN	46



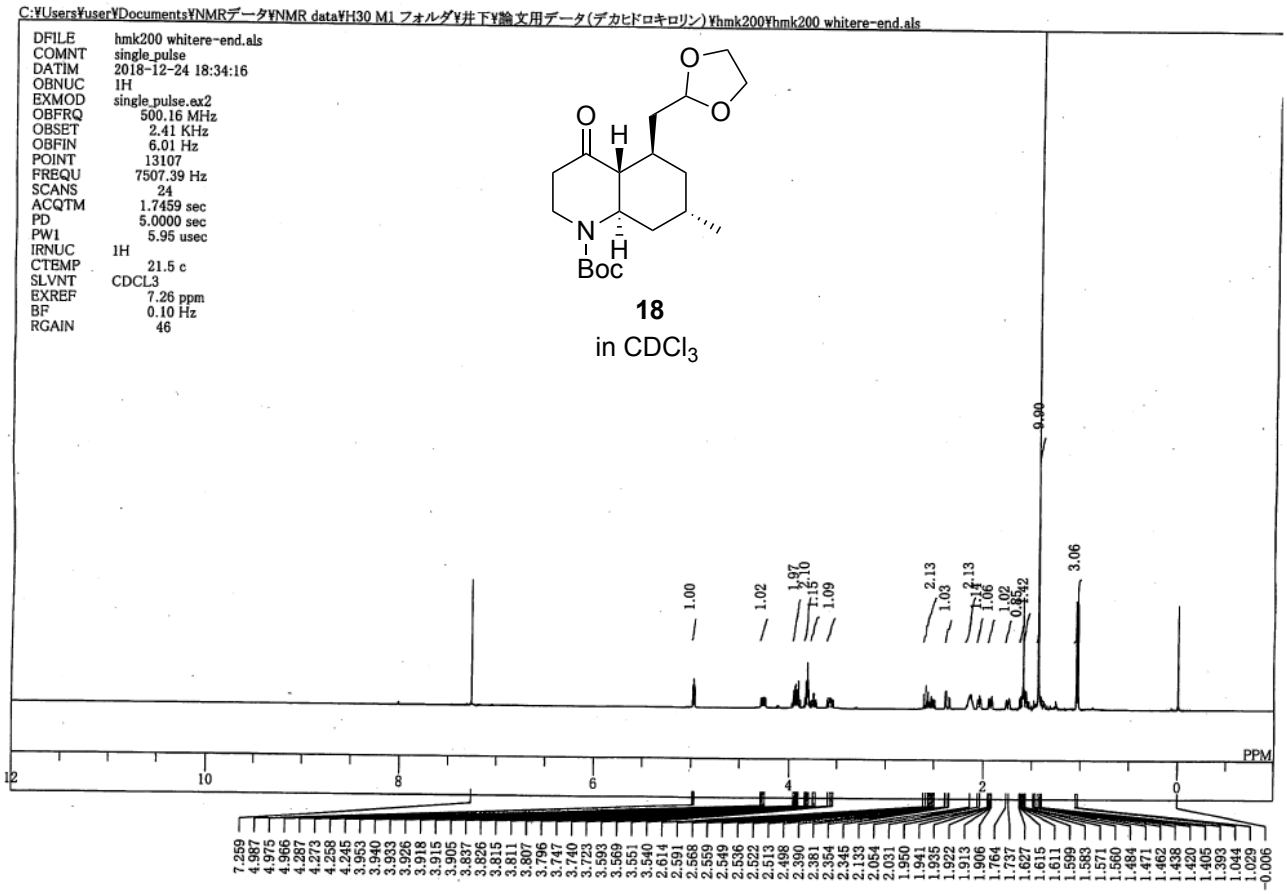
17
in pyridine-d_5

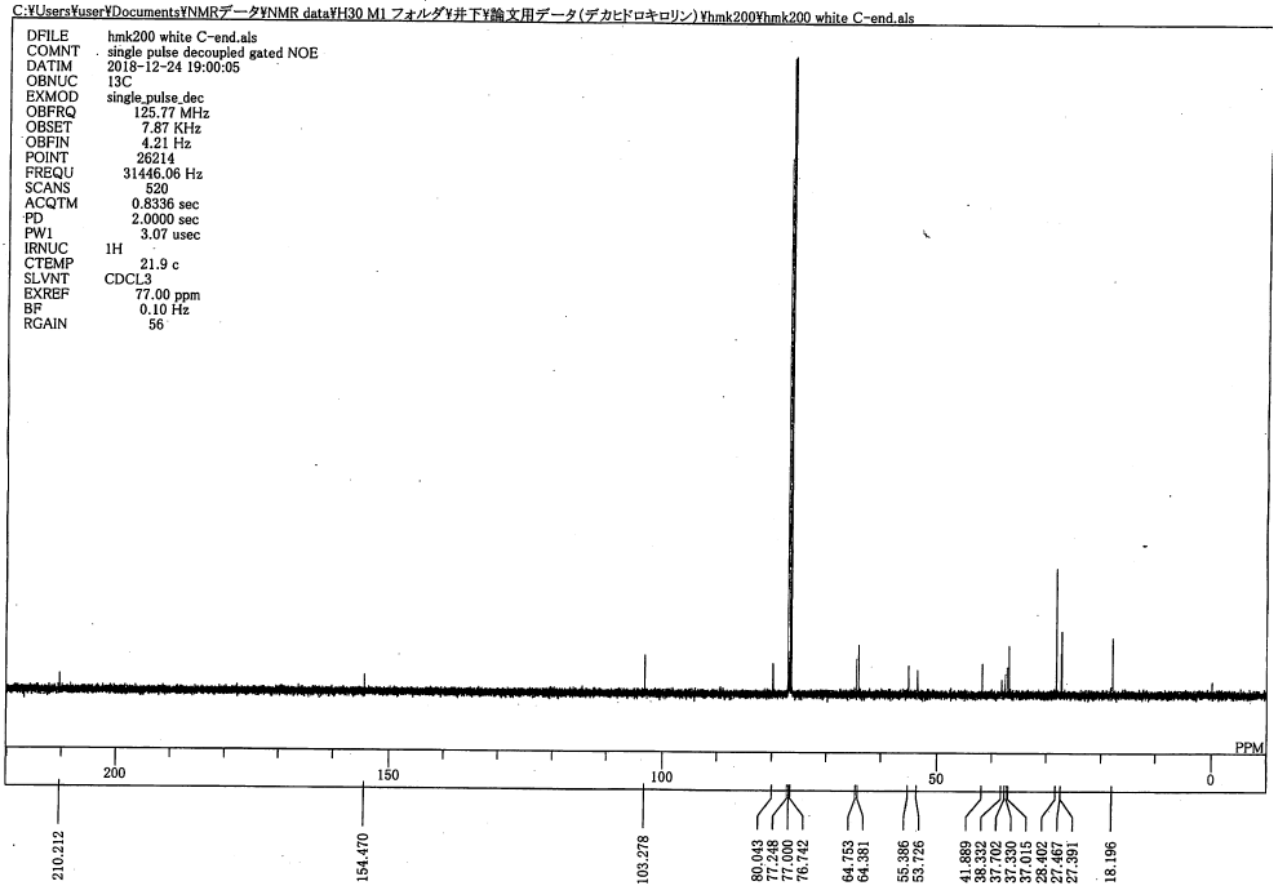
C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥208¥pyri¥hmk208 pyri noe Me2-end.als

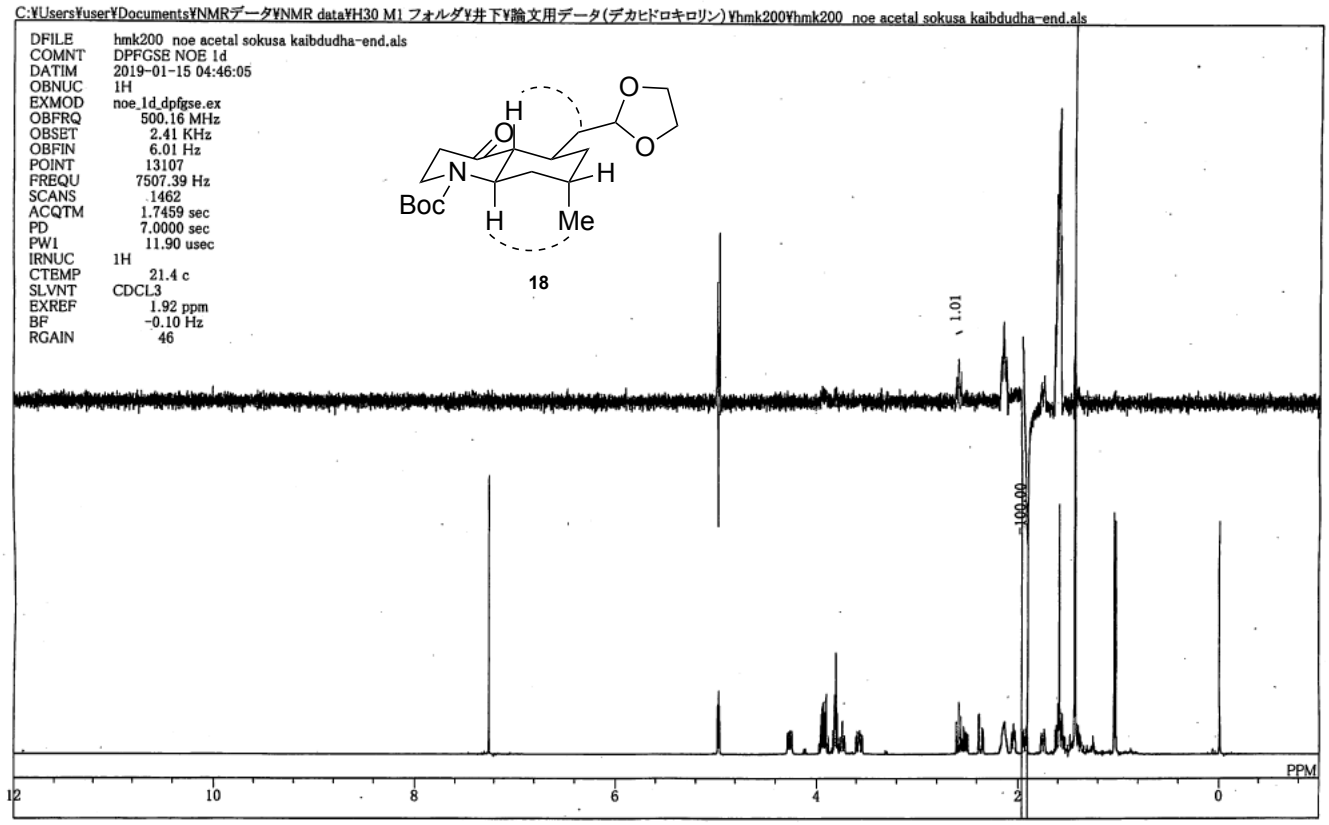
DFILE	hmk208 pyri noe Me2-end.als
COMNT	DPFGSE NOE 1d
DATIM	2019-03-01 06:08:09
OBNUC	1H
EXMOD	noe_1d_dpfgse.ex
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	3240
ACQTM	1.7459 sec
PD	7.0000 sec
PW1	11.90 usec
IRNUC	1H
CTEMP	95.0 c
SLVNT	C5D5N
EXREF	1.00 ppm
BF	0.12 Hz
RGAIN	46



17


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk200¥hmk200 whitere-end.als
DFILE hmk200 whitere-end.als
COMNT single_pulse
DATIM 2018-12-24 18:34:16
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 24
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 46
O
O
O
H
N
H
Boc
18
in CDCl3
9.00
3.06
2.13
2.13
1.97
1.15
1.10
1.09
1.03
1.06
1.02
1.00
1.02
0.83
0.82
PPM
12
10
8
6
4
2
0
7.259
4.987
4.975
4.966
4.287
4.273
4.258
4.245
3.953
3.940
3.933
3.926
3.918
3.915
3.905
3.837
3.826
3.815
3.811
3.807
3.796
3.747
3.740
3.723
3.593
3.569
3.551
3.540
2.614
2.591
2.568
2.559
2.549
2.536
2.522
2.513
2.498
2.390
2.381
2.354
2.345
2.133
2.064
2.031
1.950
1.941
1.935
1.922
1.913
1.906
1.764
1.737
1.627
1.615
1.611
1.599
1.583
1.571
1.560
1.484
1.471
1.462
1.438
1.420
1.405
1.393
1.044
1.029
-0.006


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk200¥hmk200 white C-end.als
DFILE hmk200 white C-end.als
COMNT single pulse decoupled gated NOE
DATIM 2018-12-24 19:00:05
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 520
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 56
PPM
200
150
100
50
0
210.212
154.470
103.278
80.043
77.248
77.000
76.742
64.753
64.381
55.386
53.726
41.889
38.332
37.702
37.330
37.015
28.402
27.467
27.391
18.196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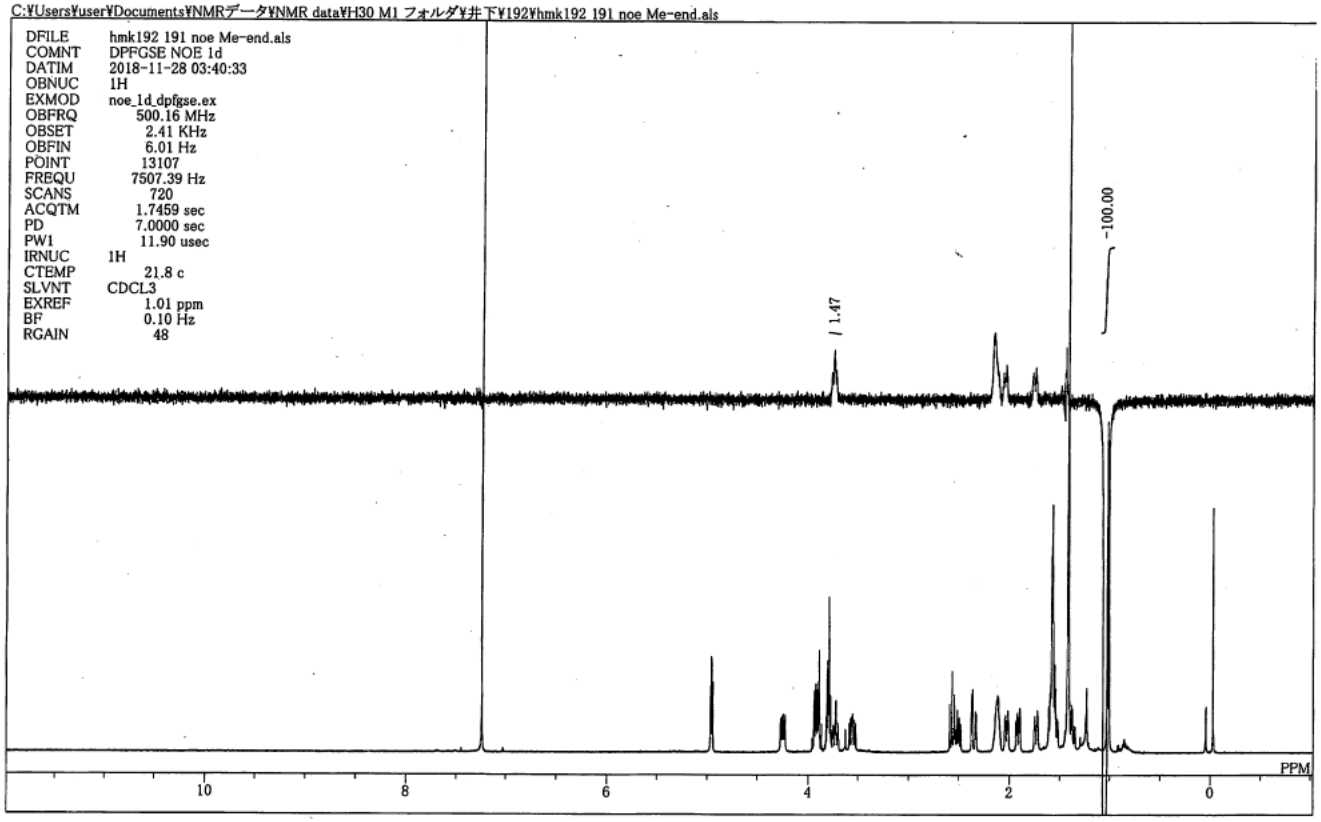
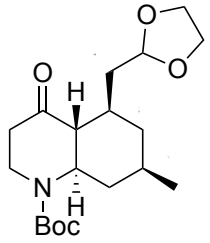
DFILE hmk200 noe acetal sokusa kaibdudha-end.als
COMNT DPFGSE NOE 1d
DATIM 2019-01-15 04:46:05
OBNUC 1H
EXMOD noe_1d_dpfgse.ex
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 1462
ACQTM 1.7459 sec
PD 7.0000 sec
PW1 11.90 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 1.92 ppm
BF -0.10 Hz
RGAIN 46
O
H
O
O
N
H
Boc
H
Me
18
1.01
100.00
PPM
12
10
8
6
4
2
0


C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥192¥hmk192 191 noe Me-end.als
DFILE hmk192 191 noe Me-end.als
COMNT DPFGSE NOE 1d
DATIM 2018-11-28 03:40:33
OBNUC 1H
EXMOD noe_1d_dpfgse.ex
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 720
ACQTM 1.7459 sec
PD 7.0000 sec
PW1 11.90 usec
IRNUC 1H
CTEMP 21.8 c
SLVNT CDCL3
EXREF 1.01 ppm
BF 0.10 Hz
RGAIN 48
1.47
100.00
PPM
10
8
6
4
2
0

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk205¥hmk205 ue-end.als

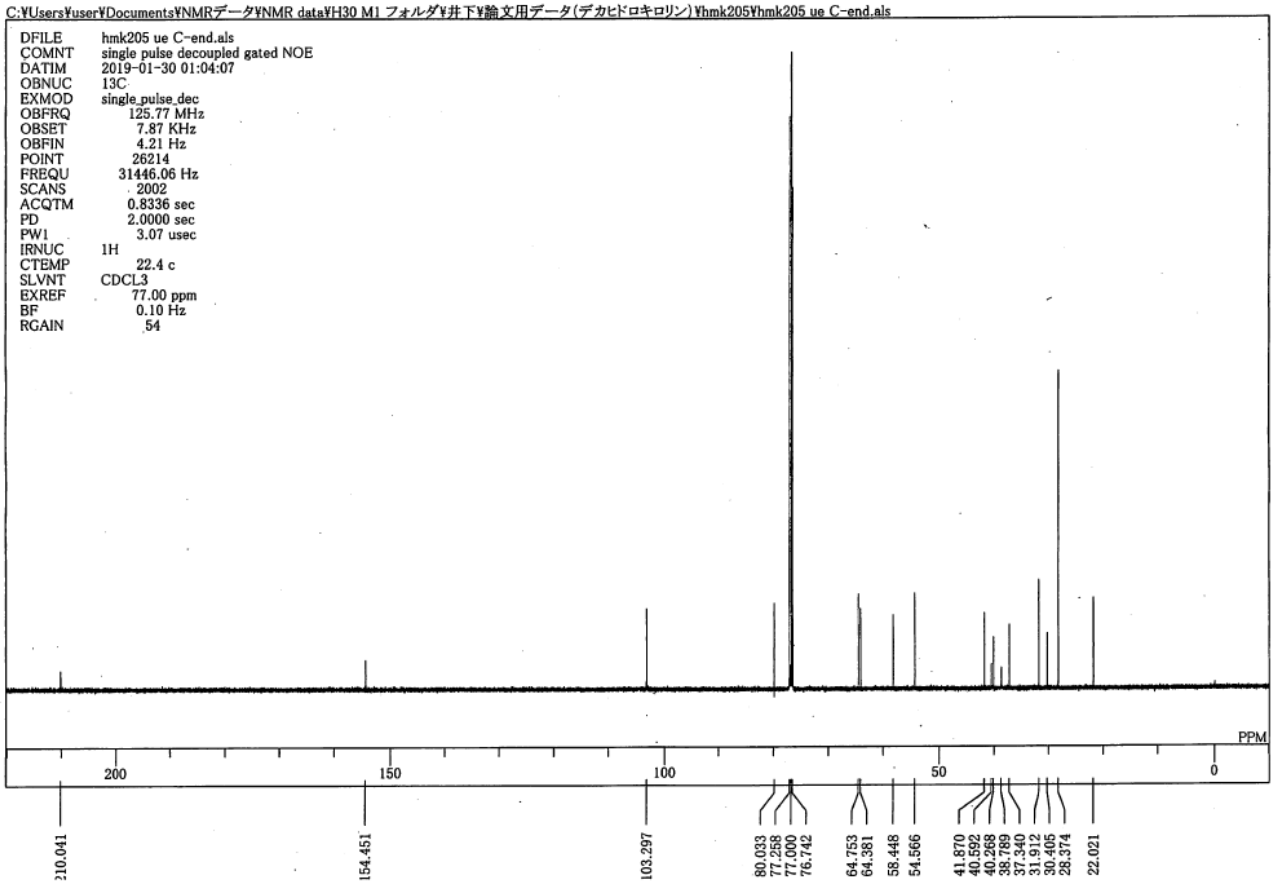
DFILE hmk205 ue-end.als
COMNT single_pulse
DATIM 2019-01-22 23:28:28
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.95 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 38

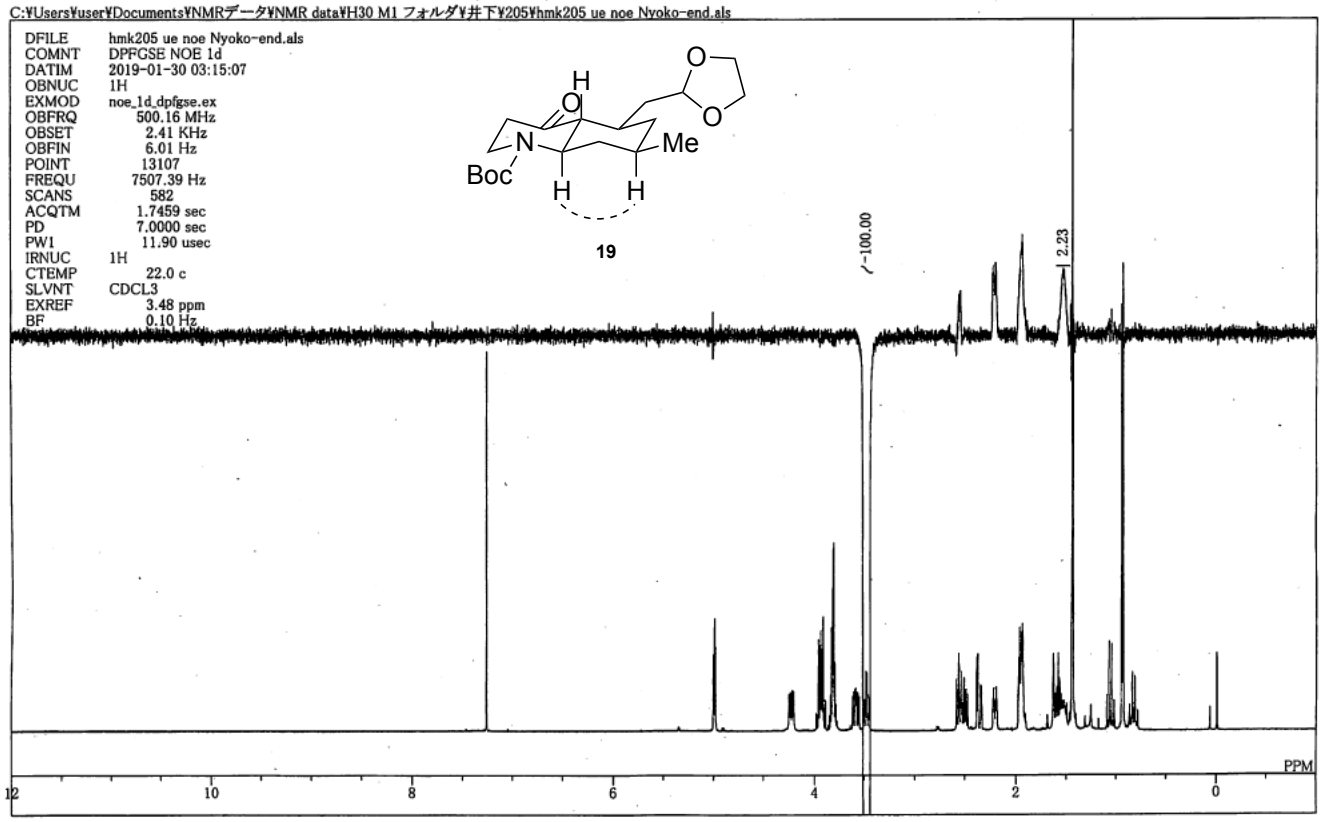


19

C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥論文用データ(デカヒドロキロリン)¥hmk205¥hmk205 ue C-end.als

DFILE hmk205 ue C-end.als
COMNT single pulse decoupled gated NOE
DATIM 2019-01-30 01:04:07
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 2002
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.07 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 54




C:¥Users¥user¥Documents¥NMRデータ¥NMR data¥H30 M1 フォルダ¥井下¥205¥hmk205 ue noe Nyoko-end.als
DFILE hmk205 ue noe Nyoko-end.als
COMNT DPFGSE NOE 1d
DATIM 2019-01-30 03:15:07
OBNUC 1H
EXMOD noe_1d_dpfgse.ex
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 582
ACQTM 1.7459 sec
PD 7.0000 sec
PW1 11.90 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCL3
EXREF 3.48 ppm
BF 0.10 Hz
H
O
O
O
N
Me
Boc
H
H
19
-100.00
2.23
PPM
12
10
8
6
4
2
0